Der katalytische Isotopenaustausch des gasförmigen Sauerstoffs. XI.[1] Die Austauschreaktion der Sauerstoffatome zwischen Sauerstoff und Wasserdampf an der Oberfläche des Natrium- und Kaliumhydroxyds. (Auszug.)[2]

Von **Yosio OSUMI** und **Noriyoshi MORITA.**

(Eingegangen am 7. Januar, 1942.)

Inhaltsübersicht. Die katalytische Austauschreaktion der O-Atome zwischen gasförmigen Sauerstoff und Wasserdampf an der Oberfläche des Natrium- und Kaliumhydroxyds wird unter Benutzung des an schwerem Sauerstoff angereicherten schweren Wassers untersucht. Dabei wird festgestellt, dass an Natriumhydroxyd von 360° ab und an Kaliumhydroxyd von 290° ab eine lebhafte Austauschreaktion stattfindet und oberhalb 450° das Austauschgleichgewicht schnell erreicht wird. Die Reaktion wird mit Hilfe der Annahme erklärt, dass an der Oberfläche des in Rede kommenden Hydroxyds eine Art Peroxyd gebildet und durch den Zerfall dieses Peroxyds die Austauschreaktion herbeigeführt wird.

Einleitung. Aus den bisher von einem von uns ausgeführten Versuche kamen wir zu dem Schluss, dass die katalytische Wirksamkeit der Oxyde bzw. Hydroxyde für die Austauschreaktion zwischen gasförmigem Sauerstoff und Wasserdampf mit der zunehmenden Gruppennummer der Elemente der Oxyde bzw. Hydroxyde zunimmt, so lange als die betreffenden Elemente sich in derselben Horizontalreihe des periodischen Systems befinden und die Gruppennummer kleiner als vier bleibt.[3] So wird z.B. gefunden, dass die in Rede kommende Austauschreaktion an der Oberfläche des Oxyds des Titans, das zur 4. Gruppe a der 4. Horizontalreihe gehört, erst von 590° ab, hingegen an der Oberfläche des Calciumoxyds, das zur 2. Gruppe derselben Horizontalreihe gehört, schon von 390° ab bemerkbar wird. Extrapoliert man diese Werte, so soll die Reaktion an der Oberfläche des Kaliumhydroxyds schon von etwa 300° ab merklich stattfinden, obwohl diese Reaktion oder im allgemeinen die Reaktion an der Oberfläche der Alkalihydroxyde noch nicht direkt experimentell untersucht wurde. Die vorliegenden Versuche wurden deshalb ausgeführt, um die betreffende Austauschreaktion an der Oberfläche der beiden typischen Alkalihydroxyde nämlich des Natrium- und Kaliumhydroxyds direkt experimentell zu untersuchen.

Versuchsmethode und -ergebnisse. Die Versuchsanordnung ist im grossen und ganzen dieselbe wie die schon früher beschriebene.[4] Das Reaktionsgasgemisch von der Zusammensetzung $H_2O:O_2=1:2$ wird aus dem an schwerem Sauerstoff angereicherten schwerem Wasser und dem elektrolytischen Sauerstoff hergestellt und dieses Gasgemisch über das in einem Katalysatorrohr befindliche und auf einer bestimmten Tem-

(1) X. Mitteil.: dies Bulletin, **15** (1940), 298.
(2) Y. Osumi und N. Morita, *J. Chem. Soc. Japan*, **62** (1941), 802.
(3) Vgl. Abb. 2 IV. Mittl. (dies Bulletin, **14** (1939), 15).
(4) N. Morita und T. Titani, dies Bulletin, **13** (1938), 357.

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peratur erwärmte Alkalihydroxyd langsam (bei Zimmertemperatur gemessen 60 ccm pro Min.) geleitet. Dabei wird das Alkalihydroxyd wegen seiner verhältnismässig leichten Schmelzbarkeit nicht als solches sondern in Verbindung mit einer Menge Asbest benutzt. Etwa 2 g von vorn herein gut gereinigter Asbest wird in 50 ccm 5 normaler Ätzalkalilösung zum Sieden erwärmt und der so mit dem betreffenden Alkali getränkte Asbest wird in dem Katalysatorrohr unter Durchleitung des Sauerstoffgases auf 400° bis zum Trocknen erhitzt.

Der aus dem Katalysatorrohr zusammen mit dem Sauerstoffgas ausgeströmte Wasserdampf wird durch Abkühlung kondensiert aufgefangen und nachdem er auf geeignetem Weg gereinigt worden ist, sein Dichteüberschuss dem gewöhnlichen Wasser gegenüber schwebemetrisch bestimmt. Bezeichnet man den so bestimmten Dichteüberschuss des schweren Wassers nach dem Versuche mit Δs_e und den vor dem Versuch d.h. ohne Austausch mit Δs_a, so lässt sich das prozentuale Austauschmass $\%A$ für die Austauschreaktion, die unter den angegebenen Versuchsbedingungen zwischen Wasserdampf und Sauerstoffgas stattfand, mit Hilfe der Gl. ohne weiteres berechnen:[5]

$$\%A = \frac{(\Delta s_a - \Delta s_e)}{(\Delta s_a - \Delta s_e)_\infty} \times 100 .$$

In dieser Gl. drückt $(\Delta s_a - \Delta s_e)_\infty$ solch eine Abnahme des Dichteüberschusses des schweren Wassers aus, die sich beim vollständigen Austausch ergeben würde. Dieser extreme Wert der Dichteabnahme des schweren Wassers $(\Delta s_a - \Delta s_e)_\infty$ kann aber nun unter Benutzung der Zusammensetzung des Reaktionsgasgemisches sowie des Gehaltes des Sauerstoffgases und Wasserdampfes an schwerem Sauerstoff rechnerisch ermittelt werden. So ergab sich unter den vorliegenden Versuchsbedingungen[6] $(\Delta s_a - \Delta s_e)_\infty = 29.1\ \gamma$. Das prozentuale Austauschmass $\%A$ in der letzten Spalte der Tabellen 1 bis 3 wird deshalb mit Hilfe der Gl. berechnet:

$$\%A = \frac{(\Delta s_a - \Delta s_e)}{29.1} \times 100 .$$

Tabelle 1. Natriumhydroxyd (Präparat A).

Versuchs-nr.	Temp. °C	$(\Delta s_a - \Delta s_e)$ in γ	$\%A$
1	435	26.5	91
2	460	28.7	99
3	505	29.0	100
4	685	30.7	106

Jede Reihe der Versuche, die in Tabelle 1 bis 3 wiedergegeben ist, wird unter Benutzung des frischen Hydroxyds ausgeführt und die Versuchsnr. in jeder Tabelle gibt die zeitliche Reihenfolge der einzelnen Versuche an. Nach der Beendigung der Versuche wurde bemerkt, dass der mit Natrium-

(5) Vgl. Gl. (1) in I. Mittl. (dies Bulletin, **13** (1938), 362).

(6) Das zum Versuch benutzte schwere Wasser wurde mit Hilfe der fraktionierten Destillation des gewöhnlichen Wassers hergestellt. Deshalb rührte vom gesamten Dichteüberschuss des benutzten Wassers, der 64.7 γ betrug, 34.8 γ von der Anreicherung des schweren Sauerstoffs. Der Rest kann auf die Anreicherung des schweren Wasserstoffs zurückgeführt werden. Dagegen war der zum Versuch benutzte elektrolytische Sauerstoff um 1.6 γ leichter als der gewöhnliche Wassersauerstoff.

Tabelle 2. Natriumhydroxyd (Präparat B).

Versuchs-nr.	Temp. °C	$(\Delta s_a - \Delta s_e)$ in γ	%A
1	360	1.9	7
2	395	10.4	36
3	415	21.1	73
Versuchs-nr.	Temp. °C	$(\Delta s_a - \Delta s_e)$ in γ	%A
2	375	4.8	17
1	398	16.9	58
3	405	24.3	84
5	426	29.3	101
4	434	29.9	103

Tabelle 3. Kaliumhydroxyd.

Versuchs-nr.	Temp. °C	$(\Delta s_a - \Delta s_e)$ in γ	%A
1	310	5.0	17
2	385	23.0	79
3	535	29.9	103
4	655	30.6	105
Versuchs-nr.	Temp. °C	$(\Delta s_a - \Delta s_e)$ in γ	%A
1	320	5.7	20
2	345	9.7	33
3	380	18.2	63

hydroxyd getränkte Asbest schwach bräunlich und der mit Kaliumhydroxyd getränkte schwach bläulich gefärbt war.

Diskussion der Ergebnisse. Die in Tabellen 1 bis 3 angegebenen Ergebnisse sind in nebenstehender Abb. 1 graphisch eingezeichnet. Wie daraus ersichtlich ist, findet die Austauschreaktion an der Oberfläche des Kaliumhydroxyds viel leichter als beim Natriumhydroxyd statt; die Temperatur $t(10\%)$, wo das prozentuale Austauschmass $\%A$ erst 10% erreicht, liegt beim Natriumhydroxyd bei 360°, dagegen beim Kaliumhydroxyd bei 290°. Dieser letztere Wert stimmt aber mit dem oben in der Einleitung angegebenen erwarteten Wert (300°) sehr gut überein.

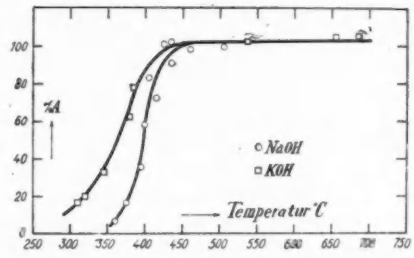

Abb. 1. Das prozentuale Austauschmass %A zwischen gasförmigen Sauerstoff und Wasserdampf an der Oberfläche des Natrium- und Kaliumhydroxyds in Abhängigket von der Temperatur.

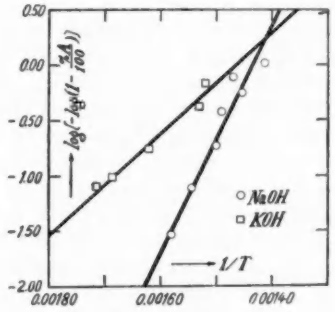

Abb. 2. Ermittelung der Aktivierungsenergie.

Der Unterschied der katalytischen Wirksamkeit zwischen Natrium- und Kaliumhydroxyd drückt sich aber noch deutlicher in der Aktivierungsenergie der betreffenden Reaktion aus. Um diese Energie zu ermitteln, wird in Abb. 2 der Logarithmus des Ausdrucks $\left[-\log\left(1-\frac{\%A}{100}\right)\right]$ gegen das Reziproke der absoluten Temperatur $1/T$ eingetragen, da dieser erstere Ausdruck der Reaktionsgeschwindigkeit proportional sein soll.[7]

(7) N. Morita, dies Bulletin, **15** (1940), 176.

Aus der Neigung der in Abb. 2 angegebenen beiden geraden Linien ergibt sich die in Rede kommende Aktivierungsenergie:

$$A(\mathrm{NaOH}) = 47 \text{ Kcal.} \quad \text{und} \quad A(\mathrm{KOH}) = 21 \text{ Kcal.} \qquad (1).$$

Gut übereinstimmend mit der aus den bisherigen Versuchen bestätigten allgemeinen Regel braucht also das weniger alkalische Natriumhydroxyd mehr Aktivierungsenergie als das stärker alkalische Kaliumhydroxyd.

Bei der Austauschreaktion an der Oberfläche der Erdalkalihydroxyde kamen wir zu dem Schluss, dass die aktivierte Adsorption des Wasserdampfes an der Oberfläche der betreffenden Hydroxyde massgebend wirkt.[8] Zieht man nun die Tatsache in Rechnung, dass der Wasserdampf an Alkalihydroxyde ebenso stark oder noch stärker als an Erdalkalihydroxyde adsorbiert wird, so ist durchaus möglich, dass die Austauschreaktion an der Oberfläche der Alkalihydroxyde nach dem ähnlichen Mechanismus wie bei den Erdalkalihydroxyden verläuft. So kann z.B. die Reaktion an Natriumhydroxyd durch folgendes Schema dargestellt werden:

$$\mathrm{NaOH(H_2O)_x + H_2O = NaOH(H_2O)_{x+1}}$$

$$\mathrm{NaOH(H_2O)_{x\ 1} + 1/2\ O_2 = NaOH(H_2O)_xH_2O_2}$$

$$\mathrm{NaOH(H_2O)_xH_2O_2 = NaOH(H_2O)_x + H_2O + 1/2\ O_2} \qquad (2).$$

Die katalytische aktive Substanz ist also kein „trocknes" Hydroxyd NaOH sondern das an diesem einige Moleküle Wasser halbchemisch verbundene „nasse" Hydroxyd bzw. eine Art Polyhydrat $\mathrm{NaOH(H_2O)_x}$. An diesem Polyhydrat wird das Wasserdampfmolekül aktiviert adsorbiert. Verbindet das so aktiviert adsorbierte Wassermolekül das Sauerstoffmolekül aus der Gasphase an sich, so wird eine peroxydartige Verbindung gebildet und bei der Abspaltung dieses Peroxyds werden die O-Atome des Sauerstoffgases gegen die des Wassers ausgetauscht.

Zum Schluss möchten wir Herrn Prof. T. Titani für die Anregung zu dieser Arbeit verbindlichst danken. Der Nippon Gakujutsu Shinkohkai (der Japanischen Gesellschaft zur Förderung der wissenschaftlichen Arbeit) sowie der Hattori Hohkohkai (der Hattori-Stiftung) für ihre finanzielle Unterstützung sind wir auch zu grossem Dank verpflichtet.

Osaka Teikoku Daigaku Rigaku-bu Kagaku Kyoshitsu
(Chemisches Institut der wissenschaftlichen Fakultät
der Kaiserlichen Universität Osaka)

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(8) N. Morita, dies Bulletin, **15** (1940), 128.

Untersuchungen über Flechtenstoffe. XCIX. Synthese der Dimethyläther-olivetonsäure und des Dimethyläther-olivetonids.(*)

Von Yasuhiko ASAHINA und Hisasi NOGAMI.

(Eingegangen am 17. Februar, 1942.)

Wie wir in einer vorläufigen Mitteilung[1] dargethan haben, ist die Jerdansche Orientierung[2] der Carboxyl-Gruppen in Dioxy-homophthalsäure und Dioxy-homo-teraphtalsäure (entstanden aus Orcin-tricarbonsäuretriäthylester durch Abspaltung eines kernständigen Carboxyls) im umgekehrten Sinne zu berichtigen. Bei der Darstellung der Orcin-tricarbonsäure-triäthylesters (I) nach Cornelius und Pechmann[3] entsteht zugleich Orcin-tricarbonsäure-diäthylester (II) vom Schmp. 141°, den Jerdan durch Kondensation von Aceton-dicarbonsäure-diäthylester in Gegenwart des Chloressigsäureäthylesters mittels Magnesiumpulvers erhielt. Derselbe Diäthylester vom Schmp. 141° lässt sich auch aus dem Orcin-tricarbonsäure-triäthylester durch konz. Schwefelsäure darstellen. Hierbei ist aber die Ausbeute sehr gering.

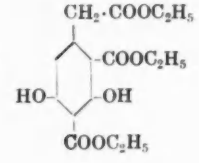
Wird der Diäthylester vom Schmp. 141° (II) mit Kalilauge erhitzt, so wird Orcin-dicarbonsäure-monoäthylester (III, R=H) vom Schmp. 190° erhalten. Vor einiger Zeit hat der eine von uns (H.N.)[4] denselben Monoaethylester über Dimethyläther-mono-äthylester-chlorid (IV, R=Cl) in Dimethoxy-carbäthoxy-phenacetylessigsäure-äthylester (V, R=H) übergeführt. Bei der Ketonspaltung des letzteren entstand die niedrigere Homologe der Dimethyläther-olivetonsäure (VI, R=H) und des Dimethyläther-olivetonids (VII, $R=CH_3$). Die Desmethyl-Verbindung der ersteren kommt nach Oxford und Raistrick[5] im Stoffwechselprodukt von Penicillium brevi-compactum vor. Die Bildung solchen Enollaktons spricht dafür, dass die Dicarbonsäure (III), nicht ein Homoterephtalsäure-Derivat (wie Jerdan glaubte), sondern ein Homophtalsäure-Derivat sein muss. Zu demselben Schluss gelangt man durch die Bildung des Orsellinsäure-äthylesters aus (III, R=H) beim Decarboxylieren.

Wird nun die Natriumverbindung des γ-(3,5-Dimethoxy-2-carbäthoxyphenyl)-acetessigsäure-äthylester (V, R=Na) mit n-Butyljodid umsetzt und das so erhaltene Butyl-Derivat (V, $R=nC_4H_9$) der Ketonspaltung unterworfen, so entsteht eine Ketosäure (VI, $R=nC_4H_9$), die sich als identisch mit Dimethyläther-olivetonsäure erweist. Beim Erhitzen mit Ameisensäure geht die letztere leicht in Dimethyläther-olivetonid (VII, $R=C_5H_{11}$) über.

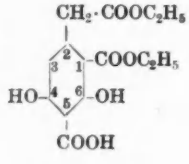
Anderseits lässt sich die Orcin-dicarbonsäure vom Schmp. 198° (VIII), die nach Jerdan[2] aus Orcintricarbonsäure-triäthylester durch

(*) Asahina u. Asano, *Ber.*, **65** (1932), 475.
(1) *Proc. Imp. Acad. Tokyo*, **16** (1940), 119; *Chem. Zentr.*, **1940** II, 1419.
(2) *J. Chem. Soc.*, **75** (1899), 808.
(3) *Ber.*, **19** (1886), 1448.
(4) *J. Pharmaceut. Soc. Japan*, **61** (1941), 56.
(5) *Biochem. Journ.* **27** (1933), 634; *Chem. Zentr.*, **1934** II, 3515.

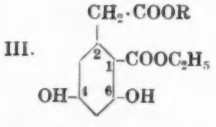
starke Kalilauge entsteht, nach folgender Unwandlung als 2.6-Dioxyhomoterephtalsäure charakterisieren. Der daraus dargestellte Dimethyläther-dimethylester (IX, R=OCH_3) (Schmp. 72–73°) liefert bei der partiellen Verseifung 3.5-Dimethoxy-4-carbäthoxy-phenylessigsäure (IX R=OH), deren Säurechlorid (IX, R=Cl) mit Natrium-acetessigester gekuppelt wird. Beim Desacetylieren des Kuppelungsprodukts bildet sich 3.5-Dimethoxy-4-carbäthoxyphenacetyl-essigsäure-äthylester (X, R=H) welcher bei der Ketonspaltung die Verbindung (XI, R=R′=H) giebt. Zufälligerweise stimmt der Schmp. der letzteren mit demjenigen des Dimethyläthers von der Raistrickschen Verbindung (VI, R=H) überein. Unsere Substanz liefert aber in keiner Weise Enollakton. Auch die aus der Verbindung (X, R=C_4H_9) erhaltene Ketonsäure (XI, R=C_4H_9, R′=H) erwies sich als nicht identisch mit Olivetonsäure und lieferte kein Enollakton.

I. 

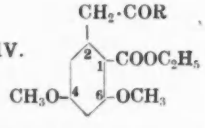
Schmp. 98°.

II. 

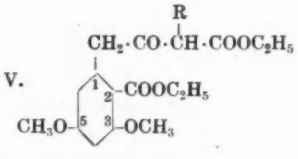
Schmp. 141°.

III. 

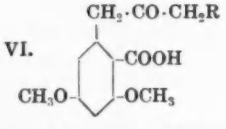
R = H, Schmp. 190°.
R = C_2H_5, Schmp. 108°.

IV. 

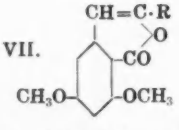
R = OH, Schmp. 103°.
R = Cl, Öl.

V. 

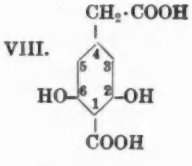
R = H, Schmp. 38.5°.
R = n·C_4H_9, Öl.

VI. 

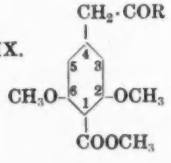
R = H, Schmp. 139–141°.
R = n·C_4H_9, Schmp. 93°.

VII. 

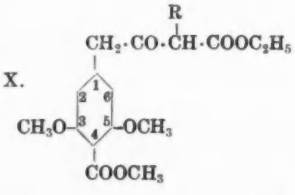
R = CH_3, Schmp. 155.5°.
R = C_5H_{11}, Schmp. 94°.

VIII. 

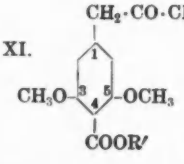
Schmp. 198°

IX. 

R = OCH_3 Schmp. 72–73°.
R = OH, Schmp. 147.5°.

X. 

R = H, Schmp. 115°.
R = n·C_4H_9, Öl.

XI. 

R = H, R′ = H, Schmp. 139–140°.
R = n·C_4H_9, R′ = H, Schmp. 137°.

Beschreibung der Versuche.

Kondensation von Acetondicarbonsäure-diäthylester mittels Natriums.[5] Man fügt 2 g. Natrium zu 200 g. abgekühltem Aceton-dicarbonsäure-diäthylester hinzu und erhitzt nach Auflösen des Metalls im Oelbad 4 Stdn. auf 140–150°. Dann schüttelt man das beim Erkalten erstarrte Produkt mit viel Benzol, wobei die Verbindung (II) teilweise ungelöst verbleibt. Um die letztere vom Triäthylester vollständig zu trennen wird die Benzollösung mit gesättigter Bicarbonatlösung (A) geschüttelt.

Orcin-tricarbonsäure-triäthylester (I): Scheidet sich beim Verdampfen der Benzollösung krystallinisch aus. Umgelöst aus Alkohol bildet er farblose Prismen vom Schmp. 98°. Ausbeute 45–50 g.

Orcin-tricarbonsäure-diäthylester-(1.2) (II): Das in Benzol schwer lösliche Kondensationsprodukt wird mit dem aus der angesäuerten Bicarbonatlösung (A) ausgeschiedenen vereinigt und aus Alkohol umgelöst. Die so erhaltene Substanz bildet farblose undurchsichtige Prismen vom Schmp. 141°. In Chloroform sehr leicht, in Alkohol und Benzol in der Wärme leicht, in Petroläther schwerlöslich. Die alkoholische Lösung färbt sich mit Eisenchlorid rotviolett, mit Chlorkalk orange. Eine Mischprobe mit dem nach Jerdan[2] dargestellten Präparat zeigte keine Schmp.-Depression. 3.605 mg. Sbst.: 7.140 mg. CO_2, 1.695 mg. H_2O. $C_{14}H_{16}O_8$. Ber. C 53.84 H 5.15. Gef. C 54.02 H 5.26

Derselbe Orcin-tricarbonsäure-diäthylester entsteht auch aus dem Triäthylester durch viertägiges Stehenlassen einer Lösung von 5 g. Triäthylester in 40 ccm. konz. Schwefelsäure. Man giesst die Schwefelsäure-Lösung im Eiswasser, extrahiert das ausgeschiedene mit Aether und schüttelt die Aether-Lösung mit Bicarbonatlösung. Im Aether bleibt 1.6 g. Ausgangsmaterial zurück. Die Bicarbonatlösung fällt beim Ansäuern ein Säure-Gemisch, woraus sich beim Fraktionieren aus Alkohol etwa 0.5 g. Orcin-tricarbonsäure-diäthylester vom Schmp. 141° isolieren lässt. In der Mutterlauge desselben befindet sich eine bei 173° schmelzende Substanz von unbekannter Struktur.

Bildung des Orsellinsäure-äthylester aus dem 4,6-Dioxy-homophtalsäure-monoäthylester-(1) (III), R=H. 0.35 g. Verb. (III R=H) werden mit 0.1 g. Kupfer-bronze in 4 ccm. Chinolin eingetragen und 15 Minuten auf 200–210° erhitzt. Das so erhaltene decarboxylierte Produkt bildet beim Umlösen aus kochendem Wasser farblose Prismen vom Schmp. 131–2°. Eine Mischprobe mit dem Orsellinsäureäthylester zeigt keine Schmp.-Depression.

Dimethyläther-olivetonsäure und -olivetonid. *γ-(3,5-Dimethoxy-2-carbäthoxy-phenyl)-α-n-butyl-acetessigsäure-äthylester* (V, R=n C_4H_9): 1.67 g. γ-(3,5-Dimethoxy-2-carbäthoxy-phenyl)-acetessigsäure-äthylester (V, R=H) werden in 10 ccm. Alkohol gelöst und unter Zusatz von 0.11 g. Natrium (gelöst in 6 ccm. Alkohol) und 1.4 g. n-Butyljodid 4 Stdn. gekocht. Dann wird das Lösungsmittel abdestilliert, der Rückstand mit Wasser umgerührt und ausgeäthert. Das beim Verdampfen des Aethers verbleibende, rohe n-Butyl-Derivat bildet ein Oel, dessen alkohol. Lösung sich mit Eisenchlorid nicht färbt. Ausb. 1.5 g.

Dimethyläther-olivetonsäure (VI, R=n-C_4H_9): Man kocht 0.5 g. oben erhaltenes n-Butyl-Derivat ca. 2 Stdn. in 20 c.c. Alkohol (90%) unter Zusatz von 1 g. Kaliumhydroxyd, destilliert den Alkohol im Vakuum, löst den Rückstand im Wasser, säuert die Lösung an und äthert das so oelig ausgeschiedene Produkt aus. Beim Umlösen zunächst aus Ligroin, dann aus Benzol-Petroläther (1:1) bildet es farblose Prismen vom Schmp. 93°. Eine Mischprobe mit der aus Mikrophyllinsäure erhalten Dimethyläther-olivetonsäure[6] zeigte keine Schmp.-Depression. 3.820 mg. Sbst.: 9.095 mg. CO_2, 2.505 mg. H_2O. $C_{16}H_{22}O_5$. Ber. C 65.27 H 7.54 Fef. C 64.92 H 7.34.

Dimethyläther-olivetonid (VII, R=C_5H_{11}): 0.1 g. VI (R=C_4H_9) wird in 5 ccm. Ameisensäure (95%) gelöst, 2 Stdn. gekocht und im Vackuum verdampft. Der Rückstand wird in Aether gelöst, die Lösung mit Bicarbonatlösung geschüttelt und ver-

dampft. Das so erhaltene, neutrale Produkt bildet beim Umlösen aus Alkohol farblose Prismen vom Schmp. 94°. Eine Mischprobe mit dem Dimethyläther-olivetonid aus der Mikrophyllinsäure zeigte keine Schmp.-Depression. 3.925 mg. Sbst.: 9.990 mg. CO_2, 2.570 mg. H_2O. $C_{16}H_{20}O_4$. Ber. C 69.52, H 7.30. Gef. C 69.42, H 7.33.

Derivate der 2,6-Dioxy-homoterephtalsäure (VIII) und deren Umwandlungen. *2,6-Dioxy-homoterephtalsäure-dimethylester*: Dargestellt durch Einwirkung von Diazomethan auf 2,6-Dioxy-homo-terephtalsäure von Schmp. 198°, die Jerdan[2] aus Orcinticarbonsäure-triäthylester beim Kochen mit konz. Kalilauge erhielt und für Dioxyhomophtalsäure hielt. Farblose Prismen vom Schmp. 77° (aus Alkohol). $C_{11}H_{12}O_6$. Ber. C 54.98 H 5.04. Gef. C 55.04, H 5.02.

2,6-Dimethoxy-homoterephtalsäure-dimethylester (IX, R=OCH_3). Dargestellt durch Kochen von oben erhaltenen Dioxy-dimethylester mit Jodmethyl und Kaliumcarbonat in Methyläthylketon. Farblose Blättchen von Schmp. 72–73° (aus Alkohol). $C_{14}H_{16}O_6$. Ber. C 58.18 H 6.01. Gef. C 57.98 H 5.98.

2,6-Dimethoxy-homoterephtalsäure-monomethylester-(1) (IX, R=OH). Dargestellt durch einstündigem Kochen von IX (R=OCH_3) in alkohol. Kalilauge. Farblose Blättchen vom Schmp. 147.5° (aus Benzol). $C_{12}H_{14}O_6$. Ber. C 56.67 H 5.55. Gef. C 56.98 H 5.29.

2,6-Dimethoxy-homoterephalsäure-chlorid-(4)-methylester-(1) (IX, R=Cl). Dargestellt durch Lösen von IX (R=OH) in Phosphor-trichlorid, Abgiessen nach gelindem Erwärmen und längerem Stehen von abgeschiedener Phosphorigsäure und Fällen durch Zusatz von Petroläther. Farblose Krystalle, die ohne weiteres zur folgenden Umwandlung verwendet wird.

γ-(3,5-Dimethoxy-4-carbmethoxy-phenyl)-acetessigsäure-äthylester-(1) (X, R=H). Man kuppelt das oben erhaltene Säurechlorid mit Natriumacetessigester und entacetyliert das Kupplungsprodukt mittels Ammoniaks in Gegenwart von Ammonchlorid. Farblose Tafeln vom Schmp. 115°. Die alkohol. Lösung färbt sich mit Eisenchlorid weinrot. $C_{16}H_{20}O_7$. Ber. C 59.23 H 6.22. Gef. C 59.19 H 6.05.

3,5-Dimethoxy-4-carbmethoxy-benzyl-methyl-keton (XI, R=H, R'=CH_3). Dargestellt durch einstündigem Kochen von X (R=H) in alkoholischer Kalilauge. Farblose Prismen vom Schmp. 100.5° (aus Petroläther). $C_{13}H_{16}O_5$. Ber. C 61.87 H 6.40. Gef. C 61.83 H 6.31.

3,5-Dimethoxy-4-carboxy-benzyl-methyl-keton (XI, R=H, R'=H.). Dargestellt durch Lösen von XI (R=H, R'=CH_3) in konz. Schwefelsäure und Fällen nach 5 stündigem Stehen mit Wasser. Farblose Nadeln vom Schmp. 139–140° (aus Benzol). Auch bei 3 stündigem Kochen mit Acetanhydrid ändert es sich nicht. $C_{12}H_{14}O_5$. Ber. C 60.48 H 5.93. Gef. C 60.24 H 5.93.

γ-(3,5-Dimethoxy-4-carbmethoxy-phenyl)-α-n-butyl-acetessigester (X, R=n-C_4H_9). Man kocht die Natriumverbindung (X. R=Na) mit n-Butyljodid in Alkohol. Farbloses Oel, unlöslich in wässriger Kalilauge, färbt sich nicht mit Eisenchlorid.

3,5-Dimethoxy-4-carbmethoxy-benzyl-n-amylketon (XI, R=n-C_4H_9, R'=CH_3). Dargestellt durch Ketonspaltung von X (R=n-C_4H_9) mittels alkoholischer Kalilauge. Syrup.

3,5-Dimethoxy-4-carboxy-benzyl-n-amylketon (XI, R=n-C_4H_9, R'=H). Dargestellt durch Lösen von XI (R=n-C_4H_9, R'=CH_3) in konz. Schwefelsäure und Fällen mit Wasser. Man kann auch die Verseifung mit alkohol. Kalilauge bewerkstelligen. Farblose Prismen vom Schmp. 137° (aus Benzol). $C_{16}H_{22}O_5$. Ber. C 65.27 H 7.54. Farblose Prismen vom Schmp. 137° (aus Benzol). $C_{16}H_{22}H_5$. Ber. C 65.27 H 7.54.

(Pharmazeutisches Institut der kaiserl. Universität Tokyo.)

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(6) *Ber.* **68** (1935), 80.

Über den Nachweis von nativem Eiweiss mit *p*H-Indicatoren. II.[1]

Von Morizo ISHIDATE und Takeichi SAKAGUCHI.

(Eingegangen am 7. März 1942.)

Um den Mechanismus der Nachweisreaktion von nativem Eiweiss mit Farbstoffen näher zu studieren, haben wir nun von neuem etwa 30 verschiedene Farbstoffen, welche in bestimmtem *p*H-Bereiche einen deutlichen Farbumschlag aufweisen, mit derselben Reaktionsbedingung wie vorher untersucht. Hierbei erweisen sich die halogenierten Fluoresceinabkömmlinge, Eosin, Cyanosin, Erythrosin, Phloxin, Rose Bengale, und die halogenierten Oxyphenylmethanderivate wie Tetrabrombenzaurin und Tetrabromrosolsäure, und noch dazu Hexanitrodiphenylamin (Aurantia) als hoch empfindliche Indikatoren gegen Eiweissklassen. Dagegen auf Pepton, Aminosäuren sowohl auch auf die anderen makromolekülaren Substanzen zeigen sie weit geringere Affinität, weshalb sie fast ebenso wie das Feiglschen Reagenz (Tetrabromphenolphthaleinäthylester) zweckmässige Eiweissindikatoren darstellen (vergl. Tafel 1 bezw. 2). Die Anwendbarkeit dieser Farbstoffe zum Nachweis der Eiweissstoffe ist damit eng verbunden, dass sie bekanntlich zum Färben von Seide und zum Wolldruck Verwendung finden.

Es wird dieses Mal auch angenommen, dass die reaktionsfähigen Farbstoffe ihre Umschlagsgebiete ausnahmslos in sauerer Seite besitzen. So ist es nicht verwunderlich, dass unter den Phenolphthaleinabkömmlingen Phenolphthalein selbst (pH=8.3−10.0), sein Methylester (8.0–9.4) und Tetrabromphenolphthalein (6.8–7.8) (I) gegen Eiweiss ganz negative Reaktion ergeben, dagegen Tetranitrophenolphthalein (1.6–3.0) (III) wie auch sein Ester (1.6–3.2) (IV) eine deutliche positive Reaktion aufweisen, und Tetrabromphenolphthalein-äthylester sowie methylester (3.5–4.9) (II) sehr wertvolle Indikatoren darstellen. Dieselbe Verhältnisse weisen auch die Fluorescein-derivate und die Oxyphenylmethanfarbstoffe auf. Also in Gegensatz zu Fluorescein (3.6–5.6) und seinen Methylester (4.0–6.2) bezw. Benzaurin (6.5–8.6) und Rosolsäure (6.9–8.0) sind ihre halogenierte Abkömmlingen Eosin (VI), Eosinmethylester (VII), Cyanosin, Erythrosin u.s.w. bezw. Tetrabrombenzaurin (V) und Tetrabromrosolsäure stark reaktionsfähiger.

Der Eintritt von Halogenen bezw. Nitrogruppen in die zwei Phenolkerne befördert die Dissoziation des betreffenden Phenols, infolgedessen wird der Farbumschlag des Farbstoffs stark nach der saueren Seite hin verschoben. Wenn einmal eines der beiden Hydroxyle methyliert wird, so wandelt sich der Farbstoff in einen reaktionslosen Stoff um. Es ist daher höchst wahrscheinlich, dass dieser geförderte Dissoziationsgrad des phenolischen Hydroxyls zur Funktion der Eiweissreaktion eine wesentliche Rolle spielt. Ob das Carboxyl am Phthalsäurereste frei oder methyl-

(1) M. Ishidate und T. Sakaguchi, *Ber.*, **74** (1941), 163.

Tafel 1.

Nr.	Indikator	Umschlagsgebiet (pH) Farbe Sauer	Alkalisch	Grenzkonzentration (%) Casein	Hämoglobin	Ovalbumin	Gelatin	Verratlösung des Indik. (A = Alkohol, W = Wasser) und der geeign. Säure.
1.	Tetrabromphenolphthaleinmethylester (Aut.)	3.5 gelb	— 4.9*) blau	0.004	0.004	0.005	0.004	0.1% A 0.2 N CH_3COOH
2.	Eosin (Merck)	0.0 orange	— 3.0 rosarot	0.0025	0.0025	0.005	0.005	0.1% W 0.1 N HCl
3.	Phloxin (Merck)	1.4 farblos	— 3.6*) rot	0.0005	0.0025	0.005	0.0025	0.05% W 0.1 N HCl
4.	Cyanosin (Gruber)	1.5 farblos	— 3.0 rot	0.0005	0.0025	0.005	0.005	0.05% W 0.1 N HCl
5.	Erythrosin (Merck)	0.0 farblos	— 3.6*) rot	0.001	0.005	0.005	0.0025	0.05% W 0.1 N HCl
6.	Rose Bengale (Grüber)	2.2 farblos	— 2.8*) rot	0.001	0.0025	0.005	0.005	0.05% W 0.1 N HCl
7.	Eosinmethylester (Aut.)	1.4 farblos	— 3.0*) rot	0.005	0.005	0.005	0.005	0.1% W 0.1 N HCl
8.	Jodeosin (Takeda)	0.5 orange	— 5.5*) rot	0.01	0.005	0.005	0.01	0.1% W 0.1 N HCl
9.	Tetranitrophenolphthalein (Aut.)	1.6 farblos	— 3.2*) gelb	0.02	0.02	0.02	1.0	0.1% W 0.2 N CH_3COOH
10.	Tetranitrophenolphthaleinmethylester (Aut.)	1.6 farblos	— 3.2*) gelb	0.05	0.02	0.05	0.2	0.1% W 0.2 N CH_3COOH
11.	Tetrabrombenzaurin (Aut.)	3.9 gelb	— 5.4*) blau	0.005	0.01	0.005	0.02	0.1% A 0.2 N CH_3COOH
12.	Tetrabromrosolsäure (Aut.)	2.7 gelb-orange	— 5.2*) violett	0.01	0.01	0.005	0.005	0.04% W 0.2 N CH_3COOH
13.	Aurantia (Grüber)	1.5 gelb	— 2.8*) orange	0.001	0.0025	0.005	0.005	0.05% W 0.1 N HCl

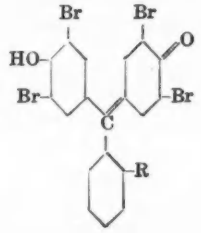
*) Das Umschlagsgebiet wurde von uns colorimetrisch mit der Pufferlösung bestimmt.

Tafel 2.

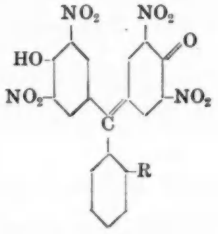
Indikator Nr.	Grenzkonzentration (%) Pepton	Glycylglycin	Glykokoll	Phenylalanin	Tyrosin	*l*-Tryptophan	Seife	Gummi arabicum	Stärke Agar-Agar u. Lecithine
1	0.2	0.5	5.0	0.5	0.1	0.25	0.5	2.0	2.0 (—)
2	0.2	1.0	2.0	1.0	0.7	0.05	0.5	0.5	2.0 (—)
3	0.05	0.25	1.0	1.0	0.1	0.25	1.0	0.25	2.0 (—)
4	0.05	0.1	0.5	0.5	0.25	0.05	0.5	0.25	2.0 (—)
5	0.05	0.5	2.0	1.0	0.3	0.25	0.5	0.25	2.0 (—)
6	0.05	0.25	1.0	1.0	0.25	0.25	0.5	0.5	2.0 (—)
7	0.05	2.5	2.0	1.0	0.1	0.1	0.5	0.5	2.0 (—)
8	0.1	5.0	2.0	1.0	0.25	0.1	2.5	2.0	2.0 (—)
11	0.25	2.0	5.0	1.0	1.0	1.0	1.0	1.0	2.0 (—)
12	0.1	1.0	1.0	1.0	1.0	0.5	0.2	0.5	2.0 (—)
13	0.1	0.5	1.0	1.0	0.025	0.05	0.5	0.5	2.0 (—)

(—): Zeigt eine ganz negative Reaktion bei der betreffenden Konzentration.

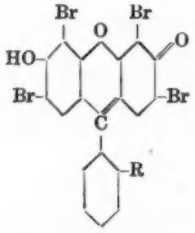
iert, ob der Phthalsäurerest halogeniert ist oder nicht, übt keinen nennenswerten Einfluss auf das Wesen der Reaktion, mit der Voraussetzung davon, dass duch Esterifizierung des Carboxyls der Umschlagsbereich des betreffenden Farbstoffs sich nicht weiter hin verschiebt, was in der Regel der Fall ist. Überdies dass das Vorhandensein von der Carboxylgruppe am Phthalsäurerest funktionell wenige Bedeutung hat, ist daraus ersichtlich, dass bromierte Benzaurin und Rosolsäure sich auch als die stark reaktionsfähigen Farbstoffe vorstellen.



I: R = COOH
II: R = $COOCH_3$
V: R = H

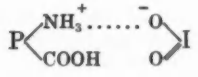


III: R = COOH
IV: R = $COOCH_3$



V: R = COOH
VII: R = $COOCH_3$

In der vorigen Abhandlung[1] haben wir schon die Annahme geäussert, dass die Reaktionsintensität zwischen Protein und Indikatoren viel mehr mit dem dissozierten Anteil des gelösten Proteinmoleküls als mit der gesammten Konzentration der beiden Komponenten in Zusammenhang steht. Hiermit kann man den Mechanismus der Reaktion so erklären, dass sich der alkalisch gefärbte Fafbstoff vornehmlich an der Stellung seines dissozierten Anions (Phenolanion und derartigen) mit dem kathionischen Zentrum des dissozierten Eiweismoleküls verbindet, wobei die Bindung genug beständig ist, in mässig saurer Lösung noch einen ursprünglichen alkalischen Farbton zu behalten. Die Bindungsform dürfte wohl folgendermassen als eine ionische Verbindung angesehen werden sein, die einen verhältnismässig schwachen Dissoziationsgrad besitzen.



P: Proteinrest
I: Indikatorrest

Bei der Ausführung der Tüpfelreaktion sauert man in der Regel das gemisch von Eiweisslösung und Farbstoffen an. Sauert man dagegen Eiweisslösung zuerst an und fügt dann Farbstoffe hinzu, so wird die Empfindlichkeit der Reaktion stark verringert. Diese Tatsache würde für die erwähnte Erklärung eine wertvolle stütze liefern können.

Fast alle genannten Eiweissindikatoren zeigen auch eine ähnliche Affinität sowohl gegen kolloidale Silber-halogenide und-cyanide, als auch gegen Silberion selbst. Es ist bekannt, dass Flourescein,[2] Dichlorfluorescein[3] und Eosin[2] bei Argentmetrie zum Adsorptionsindikator Anwen-

(2) Fajans u. Wolff, *Z. anorg. allg. chem.*, **137** (1924), 221.
(3) Kolthoff u. Laur, *J. Am. Chem. Soc.*, **51** (1929), 3273.

dung finden und zwar die letzteren zwei wohl in schwach sauerer Lösung verwendet werden. Die Eiweissindikatoren lassen sich ohne weiteres in mehr oder weniger sauerer Lösung als geeignete Adsorptionsindikatoren aufweisen, was darauf beruht, dass die am Titrationsende entstehende Verbindung $(AgCl.Ag)^+.(I)^-$ bezw. $(Ag).^+(I)^-$ in mässig sauerem Medium recht beständig ist, folglich die Lösung bezw. die Fällung am Titrationspunkt scharf angefärbt wird. Über deren praktische Anwendung werden wir später eingehend berichten. Dieses Verhalten der Farbstoffe gegen Silbermizellen würde die Annahme weiter stützen, dass bei der Eiweissreaktion der aktive Stellung im Proteinmolekül eine positiv geladene Stickstoffgruppe ist.

Endlich wollen wir noch zufügen, dass diese Affinität des Protein moleküls mit Farbstoffen, wenn auch in schwächeren Grad, auch nach Desaminieren mittels Salpetrigsäure erhalten bleibt.

Beschreibung der Versuche.

1. **Bestimmung der Grenzkonzentration der Eiweissarten** (*Tafel 1*). Die Bestimmung wurde wie vorher mittels der Tüpfelreaktion durchgeführt. Tetrabromphenolphthalein (Umschlagsgebiet pH=6.8–7.8), Phenolphthaleinmethylester (8.0–9.4), Fluorescein (3.6–5.6), Fluoresceinmethylester (4.0–6.2) lassen sich gegen 0.2% Ovalbumin, Casein und 1% Gelatin-lösung, und Benzaurin (6.5–8.6), Rosolsäure (6.9–8.0) und Dichlorindophenol (4.2–6.3) gegen 1% Ovalbumin, Casein, Hämoglobin und 5% Gelatin als reaktionsnegativ erweisen. Bei den folgenden Farbstoffreihen, die in einer sauren oder alkalischen Seite ein Umschlagsgebiet besitzen, wurde die Reaktion gegen 0.2% Ovalbumin auch als wirkungslos nachgewiesen: Alizarinrot, Anilinbraun, Benzpurpurin B, Brilliant-Kresilblau, Buttergelb, Chrysoidin, Cyanin, Hämatoxylin, Indigocarmin, Neutralviolett, Nilblau A, Orang G, Patentblau A, Protsil Sol. Pyronin G, Säurefuchsin und Wasserblau.

2. *Tafel 2.* ergibt die Grenzkonzentration des Peptons und der einigen Aminosäuren, und auch die Empfindlichkeiten gegen den einigen kolloidalen Lösungen. Wobei zeigt Pepton verhältnismässig höhere Affinität, was möglich darauf zurückzuführen ist, dass das Präparat noch gewissermassen Eiweiss enthält.

3. **Darstellung der Farbstoffen.** *Tetrabromphenolphthalin*: Dargestellt nach Baeyer[4]. Die farblose Kristalle, umgelöst mehrmal aus Alkohol, schmelzen bei 294°. (nach Baeyer: Schmp. 220–230°). $C_{20}H_{10}O_4Br_4$ Ber. Br 50.44, Gef. Br 50.48, 50.58.

Kaliumsalz des Tetrabromphenolphthaleinmethylesters: Hergestellt durch Oxydation des Tetrabromphenolphthalinmethylester mit alkalischen Ferricyankalium. Es stellt ein tief blauviolettes, in Wasser schwer lösliches Pulver dar. Das ausgangsmaterial Tetrabromphenolphthalinesters wurde durch Bromierung des Phenolphthalinesters in Eisessig dargestellt. Es stellt prismatische Kristalle von Schmp. 193° ($C_{21}H_{12}O_4Br_4$: Ber. Br 49.18, Fef. Br 49.38).

chinoid-Tetrabromphenolphthaleinmethylester-monomethyläther: Dargestellt durch Einwirkung von Diazomethan mit Tetrabromphenolphthalein methylester in der Aetherlösung. Das Substanz der Reinigung schwer zugänglich, schmilzt bei etwa 130–135° u. Zers., $C_{22}H_{14}O_4Br_4$: Ber. Br 48.29, Gef. Br 44.14.

Tetranitrophenolphthaleinmethylester. Phenolphthalinmethylester wurde mit konz. Schwefelsäure und Salpetersäure behandelt. Beim Zusatz von Wasser scheidet der Nitrokörper ab, der beim Umlösen aus Eisessig einen gelblichen feinen Kristall von Schmp. 266° liefert. $C_{21}H_{12}O_{12}N_4$ Ber. N 10.94, Gef. N 11.26.

(Pharmazeutisches Institut der kaiserl. Universität Tokio.)

(4) *Ber.*, **9** (1876), 1231.

Studies on the Reactions between Oxides in Solid State at Higher Temperatures. VI.[1] Discussion of the Reaction Mechanism with a Special Reference to the Effect of Particle Size on the Reactions.

By Yasuo TANAKA.

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Introduction. In the present series of investigations, the author has studied several examples of the addition reactions between so-called basic and acidic oxides in the solid state at relatively high temperatures. The experiments have been carried out with the mixtures of two components, consisting of fine powders. The method of investigations was as follows: after the addition compounds, formed by the solid reactions, had been confirmed, the courses of the reactions were followed analytically by the difference of solubility of the components as well as that of the reaction products, and the results were checked by means of the X-ray method. Since the course of the reaction between MgO and TiO_2 had been proved to be the same under various experimental conditions, the other reactions were studied only with the pressed bodies of the powder mixtures. As these reactions take place only at high temperatures, it is difficult to follow the course of reaction quantitatively by the so-called Tubandt's method,[2] which determines the exchanged amount at the contact plane of the two solid substances after the reaction and which has been applied for the reactions between metals or between certain salts.

As for reaction between solid substances, it has been considered in the first report[3] that an amorphous layer of the mixture of the components is formed at first at their contact surface; that a new reaction product crystallizes out easily from this mixture, so long as the reaction temperature is sufficiently high; and that the later reaction proceeds by the diffusion of the components through this crystalline layer.[4] If the surface reaction takes place rapidly enough, comparing with diffusion, the step that determines the rate of the whole reaction lies in the diffusion process, and many solid reactions have been regarded to be controlled by this process.[5]

The mechanisms of the present reactions had been discussed to some extent in the first report as well as in the others, and it was estimated that the rates of these reactions were also determined chiefly by the dif-

(1) V, *this Bulletin*, **17** (1942), 186.

(2) *Cf.* C. Tubandt, "Handbuch der Experimentalphysik," Bd. XII, 1. Teil, Leipzig (1932).

(3) I, this Bulletin, **16** (1941), 428.

(4) *Cf.*, for instance, W. Jost, "Diffusion und chemische Reaktion in festen Stoffen," 39, 180, etc., Dresden and Leipzig (1937).

(5) *Cf.* G. F. Hüttig, *Z. angew. Chem.*, **49** (1936), 882; W. Jander, *Z. angew. Chem.*, **49** (1936), 879; J. A. Hedvall, "Reaktionsfähigkeit fester Stoffe," 146, etc., Leipzig (1938).

fusion process. However, these reactions were proved to have their own characteristics, and it was expected that there existed something different in their reaction mechanisms.

The present paper aims at dealing with the mechanism of these reactions in more detail, by studying theoretically as well as experimentally the effect of the particle size of each of the components on the reactions.[6] Further, the mechanism of sintering due to the solid reactions is discussed.

I. Types of Reactions. The main characteristics of the reactions studied are summarized in Table 1. Though each of the characteristics has been explained on separate occasions, some of them will be repeated here.

Table 1. Main Characteristics of the Reactions in the Present Investigations.

Reaction system	Addition compound	Solid solution range	Compound or solid solution formed at first	"Reaction temperature" (°C)	Initial reaction	Heat of** activation Kcal./mole
$MgO-TiO_2$[3]	$2MgO\cdot TiO_2$, $MgO\cdot TiO_2$, $MgO\cdot 2TiO_2$	—	$MgO\cdot 2TiO_2$	725[10]	rapid	36
$CaO-TiO_2$[7]	$CaO\cdot TiO_2$	$3CaO\cdot 2TiO_2$ ~ $CaO\cdot TiO_2$* ($+TiO_2$)	$CaO\cdot TiO_2$* ($+TiO_2$)	675[10]	rapid	30.3
$MgO-Al_2O_3$[1]	$MgO\cdot Al_2O_3$	$MgO\cdot Al_2O_3$ ~ $MgO\cdot 2Al_2O_3$	$MgO\cdot Al_2O_3$	<800	rapid	41.1
$MgO-SnO_2$[8]	$2MgO\cdot SnO_2$	—	—	950	slow	100
$CaO-SnO_2$[9]	$2CaO\cdot SnO_2$, $CaO\cdot SnO_2$	—	$CaO\cdot SnO_2$	900	no	85

* Contains a slight excess of TiO_2.
** Of the formation of the first reaction product.

When a reaction is controlled by diffusion, there exists approximately a relation,[11]

$$d\xi/dt = k'/\xi \quad \text{or} \quad \xi^2 = 2k't + \text{const.}, \qquad (1)$$

where ξ is the thickness of the reaction product and t, the reaction time. If the reaction, with powder mixtures, is assumed to proceed uniformly on the particles of a spherical substance with a radius of r,

(6) It may not be amiss to mention here that the author's purpose is not to present in this paper unique and quantitative discussions, but rather to offer some suggestive mechanisms of the reactions which are consonant to the experimental results obtained.
(7) II, this Bulletin, **16** (1941), 455.
(8) III, this Bulletin, **17** (1942), **64.**
(9) IV, this Bulletin, **17** (1942), 70.
(10) G. Tammann, *Z. anorg. allgem. Chem.*, **149** (1925), 68.
(11) H. Braune, *Z. physik. Chem.*, **110** (1924), 147; W. Jost, *loc. cit.*, 15, 30.

$$1-\sqrt[3]{1-x} = \xi/r$$

hold between ξ and x, the reaction amount per unit substance at a given time.[12] Therefore, we obtain

$$\{1-\sqrt[3]{1-x}\}^2 = \frac{2k'}{r^2}t\,, \qquad (2)$$

or

$$\{1-\sqrt[3]{1-x}\}^2 = 2kt\,. \qquad (3)$$

The rates of the main parts of these reactions were expressed by this equation, and accordingly it was pointed out, as above mentioned, that they were controlled by diffusion.

However, in the three systems, MgO–TiO_2, CaO–TiO_2 and MgO–Al_2O_3, the reaction proceeded within a half an hour from the commencement of the reaction, more rapidly than the rate expressed by equation (3); the reaction between MgO and SnO_2 proceeded slowly at first, especially at lower temperatures, namely, rather an induction period was observed in this case; while in the reaction between CaO and SnO_2, the above equation was held from the beginning.

Further, when the energy of activation, Q, of the diffusion process was calculated from the temperature coefficient of the velocity constant according to

$$k = Ae^{-Q/RT}\,, \qquad (4)$$

it was found that the values for the three former reactions lay approximately between 30 and 40 Kilocalories per mole, while those for the last two were 100 and 85 Kilocalories, respectively. Thus the energies of activation of the last two reactions were twice to three times greater than those of the former ones.

The effect of temperature on these reactions can also be seen dis-

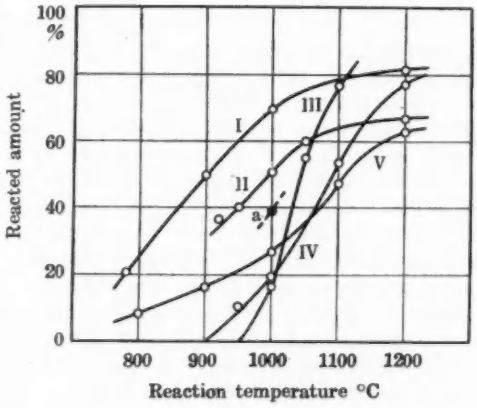

Fig. 1. Reacted amounts at various temperatures.

Curve I: The amount at a half an hour with a mixture, $MgO:TiO_2 = 1:2$, calculated from unreacted TiO_2.[7][13]

Curves II–V: The amounts at three hours, respectively, with the mixtures, $CaO:TiO_2 = 1:1$, calculated from free CaO;[7] $MgO:SnO_2 = 2:1$[8] and $CaO:SnO_2 = 1:1$,[9] calculated from soluble SnO_2; and $MgO:Al_2O_3 = 1:1$, calculated from free MgO.[1]

(12) W. Jander, *Z. anorg. allgem. Chem.*, **163** (1927), 1.

(13) As the preparations were used without heat treatment in this experiment, the reaction took place very easily. Under similar conditions as in the other reactions, the reacted amount at 3 hours falls on the point a.

tinctly from the reaction amounts at a certain reaction time given in Figure 1. The reaction takes place moderately already at as low as 800° in the systems, $MgO–TiO_2$, $CaO–TiO_2$ and $MgO–Al_2O_3$, while the reaction temperature,[10] or the temperature at which the first evidence of the reaction is observed, of the systems $MgO–SnO_2$ and $CaO–SnO_2$, lies at 950° and 900°, respectively; nevertheless, the increase of the reaction rate with the temperature is very remarkable in the latter two reactions.

From these facts, the reactions studied here can be classified into two types: (1) the reactions of the three systems, $MgO–TiO_2$, $CaO–TiO_2$ and $MgO–Al_2O_3$, in which a rapid initial reaction and a small energy of activation are observed, and (2) those of the systems, $MgO–SnO_2$ and $CaO–SnO_2$, which have an induction period rather than a rapid initial reaction and a large energy of activation. It is easily expected that there should exist a certain relationship in the differences of the initial states of these reactions and their energies of activation.

II. Considerations on the Initial States of the Reactions. Surface Diffusion and Inner Diffusion. The initial states of these reactions will be considered at first. It is true, as has been stated in the first report,[3] that the reaction heat is one of the causes for a rapid initial reaction, but an induction period can not be explained from this consideration. The difference in the initial states may be interpreted as follows:

Although the relation (3) is derived approximately by assuming that a reaction with powder mixture proceeds uniformly on a spherical substance, the experimental conditions do not strictly correspond to the assumption, because the particles of the components are by no means in contact with each other completely at the commencement of the reaction, however fine the preparations may be. The reaction begins only at the contact points of the components, and therefore, it takes place but slightly at the beginning. As the reaction proceeds, the product is formed from these contact points in the particles of both components. At the same time, however, the product tends to diminish its own surface area, because the crystals of the product at this stage are not yet fully developed, or in a state of disorder and have a large surface energy;[5] a diminution of the surface area results in the increase of the interface of the components, and consequently the reaction rate increases gradually.

Now we shall consider a mixture of components, A and B, consisting of spherical particles in which all particles of A are surrounded completely by B, e.g., a mixture with a large excess of B. The total surface of A is covered more rapidly with the reaction product than that of B; and after the thickness of the product on A becomes approximately uniform, a further reaction proceeds with a constant rate. Then equation (3) becomes valid for A, or generally, for the component of which surface area is smaller.[14] Thus an induction period should be observed at the beginning of the reaction. Assuming that a volume change due to the reaction is to be neglected and that the product is formed in both component particles with nearly equal quantities, the course of reaction is represented schematically in Figure 2 as t_1, τ and t_2.

(14) The total surface area of a given component in an unit reaction mixture will be frequently denoted simply as "surface area".

The present investigations have been carried out with the mixtures, compositions of which are corresponding to, or not too far from those of the reaction products. With these mixtures, if the particles of both components are assumed to be of equal size, about a half of the particles which surround each particle of a given component consists of its own; therefore, it should require a longer time before the particles are covered completely with the reaction product and the reaction begins to proceed uniformly. However, if the particles consist of different sizes, as it occurs practically, they will be in contact with each other more closely, and a uniform reaction may be observed comparatively readily. This condition is especially well satisfied in the present experiments, because they have been carried out with the pressed bodies. In these instances, equation (3) would be approximately applicable for both of the components.

So far it has been considered that the diffusion takes place only through the reaction product; however, it occurs also in another way, namely, one of the components can migrate on the surface of the reaction product as well as that of the other component. These two kinds of dif-

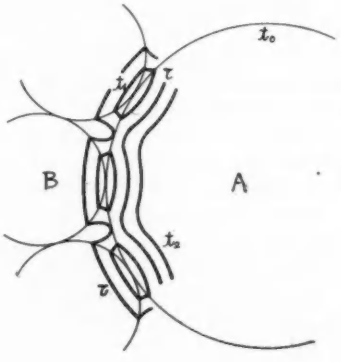

Fig. 2. Course of the reaction without surface diffusion (model).

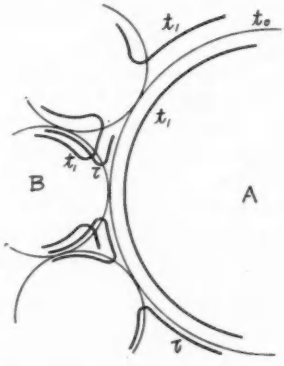

Fig. 3. Course of the reaction with a rapid surface diffusion (model).

fusion may be termed as the inner diffusion and the surface diffusion. It has been known that in metals the surface diffusion takes place more readily than the inner diffusion.[15] Moreover, there are many instances of the solid reactions between oxides which take place smoothly in the temperature range still lower than that of the present experiments, and they have been regarded to proceed chiefly by the surface diffusion at these temperatures.[16]

Therefore, let us consider a reaction in which the component B migrates on the reaction product, and, further, on A far more readily than it suffers the inner diffusion. When the components consist of very fine powders, as have been used in the present experiments, the reaction

(15) I. Langmuir, *Chem. Rev.*, **13** (1933), 147; *J. Franklin Inst.*, **217** (1934), 543.
(16) J. A. Hedvall and G. Cohn, *Kolloid Z.*, **88** (1939), 224.

proceeds considerably at its early stage of the reaction owing to the surface diffusion. After the surface of A is covered completely by B, the inner diffusion proceeds uniformly on A; and, as the step that determines the rate lies also in the inner diffusion, equation (3) holds for A, or the diffused component.[17] In this case, therefore, a rapid initial reaction should be obtained. (It is considered that the part of a particle of A which is not surrounded by B, and even a particle which is not at all in contact with B, is covered gradually by B.) The course is shown schematically in Figure 3. In this case, the size of A particles increases with the reaction, while that of B decreases and disapppears finally.

According to the above considerations, a rapid initial reaction rate, found in the reactions of the three systems, MgO–TiO_2, CaO–TiO_2 and MgO–Al_2O_3, may be explained as to be due to the rapid surface diffusion; and the induction period of the reaction between MgO and SnO_2, as the absence of the distinct surface diffusion. There may exist such an intermediate case in which the surface diffusion takes place slowly and compensates the induction period of the inner diffusion, and equation (3) holds apparently from the beginning of the reaction. The reaction between CaO and SnO_2 is probably an example of this case.

III. Discussions on the Effect of Particle Size of the Components on the Reactions. The relation between the surface phenomenon and the inner diffusion can be more distinctly understood when the effect of particle size of the components on the reactions is considered.[18]

There exists the relation (2) between the reaction amount and the particle size, and, by the reaction between $BaCO_3$ and SiO_2 with a mixture of $BaCO_3$:SiO_2=1:10, Jander[12] has proved experimentally the validity of the relation by changing the particle size of $BaCO_3$.[19] However, as it is discussed in the last section, equations (2) and (3) should hold for the component with a smaller surface area when only the inner diffusion occurs, and for the diffused component when the rapid surface diffusion takes place; and there exists a rapid or a slow initial reaction period before these relations become applicable.

We shall discuss the effect of particle size on these reactions, taking the different cases into consideration. The radii of the two components are denoted as r_A and r_B, and for convenience, let r_B be constant, $r_{B\,0}$.

§ 1. *The Case in which no Surface Diffusion exists.* The following two instances will be discussed.

(*a*) The particles of A are surrounded completely by those of B:—In the normal reaction period[20] equation (2) holds for A. In the

(17) In this paper, "diffused" component means the component into which the other diffuses. The component that diffuses into the other will be referred to as the "diffusing" component. In Fig. 3, A is the "diffused", while B is the "diffusing" component.

(18) When we consider a powder mixture of the two components with a definite composition, their total surface areas are inversely proportional to their particle sizes.

(19) The existence of a slight induction period, which he explained in a different way from that of this paper, was observed in his experiment.

(20) The period in which the reaction proceeds owing to the inner diffusion according to equations (2) and (3) will be mentioned as the normal reaction period.

region where the reaction does not proceed too far, since the relation between the reaction amount and the thickness of the product can be expressed approximately by

$$x = 3\xi/r_A ,$$

equation (2) becomes

$$x^2 = \frac{k''}{{r_A}^2} t . \qquad (5)$$

Let τ be the initial reaction period, x_τ be the reaction amount produced in this period, and the reaction time from the commencement of the reaction be denoted as t, then we obtain from (5)

$$x = \frac{k}{r_A}\sqrt{t-\tau} + x_\tau . \qquad (6)$$

In the induction period, ξ also increases according to the relation (1), while x changes with ξ and can be expressed as

$$x = \frac{1}{r_A}\int k(\xi)d\xi , \qquad (7)$$

or

$$x = \frac{1}{r_A}\int k(t)dt . \qquad (8)$$

However, since r_B is constant, as seen from Figure 2, it is admitted that the reaction amount per one particle of A increases with ξ, or with t nearly in the same way, unless r_A is not very small; namely, in (7) and (8), $k(\xi)$ and $k(t)$ may be assumed to be independent of the particle size of A. Then τ becomes also constant, and we have

$$x_\tau = \frac{k_\tau}{r_A}\sqrt{\tau} ,$$

and equation (6) becomes

$$x = \frac{k}{r_A}\sqrt{t-\tau} + \frac{k_\tau}{r_A}\sqrt{\tau} . \qquad (9)$$

Therefore, the whole course of the reaction is expressed approximately by (8) and (9), and, throughout the induction and the normal reaction periods, there exists a relation,

$$x = K/r_A , \qquad (10)$$

between x and r_A. In other words, the reaction amount at any reaction time should be inversely proportional to the particle size of the component A.

(*b*) Equal amounts of A and B exist:—[21] When $r_A \gg r_{B\,0}$, since A becomes surrounded completely by B, the conditions in (a) are satisfied and equation (10) holds for A. Similarly, when $r_A \ll r_{B\,0}$, the same relationship holds for B, and in this case x is constant whatever r_A may be, because r_B is constant. With a medium sized particle of A, for instance, $r_A = r_{B\,0}$, as it is discussed in the last section, the particles of the two components are in contact with about a half of their own component; therefore, the reaction amount in the induction period is smaller than that which is discussed in (*a*), and it takes a longer time until the induction period is completed.

In this case, therefore, the curve in which x is plotted against $1/r_A$ at a certain reaction time changes gradually from $x = K/r_A$ to $x = \text{const.}$ in the neighbourhood of $r_A = r_{B\,0}$.

§ 2. *The Case in which remarkable Surface Diffusion occurs.*

(a) B diffuses on A, which is surrounded completely by B:—If we neglect the reaction amount due to the inner diffusion in the initial reaction period, the condition becomes just as discussed in § 1 (*a*), although the reaction amount in the initial stage is, of course, very much and this period is completed rapidly. Therefore, the course of reaction is expressed approximately by (8) and (9), and the relation (10) holds at any reaction time.

(*b*) Equal amounts of A and B exist:—When B diffuses on A, the above relations hold approximately, whatever the relation between r_A and r_B may be. Similarly, when A diffuses on B, equation (10) holds for B, and x becomes constant, whatever r_A may be. However, when r_A and r_B differ too much far and the surface area of the diffused component is far larger than that of the diffusing component, it needs a longer time until the total surface of the former is covered completely, and therefore the reaction amount at a certain reaction time, especially at the beginning of the reaction, is smaller than what is discussed above. In an extreme case, no normal reaction period is attained.

IV. Results of the Experiments on the Effect of Particle Size. The above discussions seem to have proved experimentally for the reactions of the systems, MgO–SnO_2, MgO–Al_2O_3 and CaO–TiO_2; the details of which are described in the experimental part (sections VII–IX). The experiments have been carried out with the mixtures corresponding to the addition compounds.

The results of the experiment on the reaction between MgO and SnO_2 correspond to the case of § 1 of the last section; therefore, it is concluded that the reaction proceeds, as it is expected, mainly by the inner diffusion. However, a slight tendency of diffusion of MgO on the surface of SnO_2 is also observed.

As for the reaction between MgO and Al_2O_3, it is concluded that Al_2O_3 diffuses rapidly on MgO at first, and a further reaction takes place uniformly on the surface of MgO. In the last report,[1] it was found

(21) The argument is carried out for the equal volume amounts of the components, but it is valid to a first approximation for equi-molar mixtures or for the mixtures corresponding to the addition compounds.

that this reaction proceeded more readily with the mixtures containing the excess of MgO than with the other mixtures. As the particles used at that occasion were very fine and could be regarded as nearly of equal size, the total surface of MgO per unit mixture became larger when MgO existed in excess. Since Al_2O_3 diffuses on the surface of MgO, it is understood that the reaction proceeds rapidly in this condition.

By the reaction between CaO and TiO_2, it is considered that CaO diffuses on TiO_2, while at the same time the inner diffusion takes place comparatively readily; and indeed, as it is clear from the experiment in the second report,[7] the reaction amount in the initial stage of this reaction is not so much as compared with those of the reactions, MgO–Al_2O_3 and MgO–TiO_2. It is of some interest to note that Al_2O_3, the acidic component, migrates on MgO in the reaction between MgO and Al_2O_3, while the basic component, CaO, diffuses on TiO_2 in this reaction.

In analogy to these experiments, it is admitted that the other two reactions, MgO–TiO_2 and CaO–SnO_2, proceed, respectively, as discussed in section II; and the component which migrates on the surface of the other may be regarded as MgO and CaO, respectively.

The technical importance of the effect of particle size on the reactions will be mentioned here. The solid reaction in which the surface diffusion takes place rapidly, for instance, the reaction between MgO and Al_2O_3, proceeds more readily when the diffused component is very fine; therefore, in order to obtain a certain addition compound with ease, we should endeavour to pulverize the diffused component as fine as possible rather than *vice versa*. This is particularly well understood from Figure 6 (in section VIII), where the reaction proceeds more rapidly when MgO, the diffused component, (and Al_2O_3, not necessarily) is very fine. When no distinct surface diffusion exists, it is desirable that both of the components are pulverized equally well, because the reaction rate is then controlled by the particle size of the component with a smaller surface area (or with a greater particle size); only when one of the components exists in a small quantity, this component should be fine.

V. Further Considerations on the Diffusion Mechanism. As it has been stated in the first report, Wagner[22] considered that the reactions in solid state proceed frequently by the exchange of the components in the form of ions (generally smaller metal ions), or by the "ionic diffusion", through the reaction product in which electrical neutrality is always preserved. He proved this point experimentally for the reaction between AgI and HgI_2[23] and supposed further that the analogous mechanism may hold for the formations of silicates and spinels,[22] but the experimental confirmations for the latter reactions are still lacking. On the contrary, Hedvall and Cohn[16] stated that the diffusion in such a compound as silicates or spinels, the formation of which takes place smoothly already at so low temperatures that no distinct ionic conductivity is observed, could hardly be considered as ionic; and that these reactions proceed probably by the migration of the neutral atoms, or atom groups,

(22) C. Wagner, *Z. physik. Chem.*, B, **34** (1936), 309.
(23) E. Koch and C. Wagner, *Z. physik. Chem.*, B, **34** (1936), 317.

through the defect positions of the crystals, which exist owing to the incompleteness of the crystal growth,[24] or on the "inner surface" of the crystals. This mechanism may be mentioned as the "non-ionic diffusion". Thus, no conclusion has been given on the kinds of the elementary particles which migrate in these reaction products.

It is considered that the similar solid reactions can never be explained by a single mechanism; and, indeed, by studying the exchange reactions of certain wolframates and molybdates with a group of divalent metal oxides as well as their electric conductivities, Jander[25] has considered that some of these reactions proceed by the ionic diffusion while others by the migration of the neutral acid anhydride, i.e., WO_3 or MoO_3.

Also the two types of the reactions found in the present investigations will probably be due to the differences in the nature of the reaction products as well as in their diffusion mechanism, and the author would like to explain, at present, these differences as follows:

Although the ionic conductivities of these reaction products are not yet certain, it may be assumed that they are very small at the temperature as low as 800°. The three reactions, MgO–TiO_2, CaO–TiO_2 and MgO–Al_2O_3, are then to proceed, at least lower than 800° by the non-ionic migration of the components through the product. The surface diffusion in these instances may also be explained by a similar mechanism. On the other hand, for the other two reactions, MgO–SnO_2 and CaO–SnO_2, which begin to take place at 950° and 900° respectively, the interpretation of the ionic diffusion may be possible. It is considered, namely, that the crystals of these reaction products are (when once formed) well developed, and it is difficult for the neutral atoms, or atom groups, to diffuse through them; and that they begin to dissociate with the increasing temperature, and the ions thus produced become to be able to exchange with each other. In these systems, the possibility of the ionic surface diffusion might be expected at higher temperatures; however, as Hedvall has stated,[16] the exchange of ions at the surface of the ion crystals is hardly in question.

The energies of activation obtained in the latter two reactions may be regarded as that of the ionic diffusion. At higher temperatures, the ionic diffusion in the former three may also be possible; however, it is considered that the controlling steps are still the non-ionic diffusion, and that the energies of activation obtained, which are smaller than those of the latter ones, will be those of the non-ionic diffusion.

In this way, the differences in the energies of activation of the two types of the reactions as well as the existence of the surface diffusion in the former cases can well be interpreted. However, the final conclusion on this problem should be drawn only after more examples of similar reactions have been accumulated, and especially after the physical properties of the products have been made clearer.

VI. Sintering due to Solid Reactions. The phenomenon of sintering, i.e., a phenomenon in which a solid substance shrinks and reduces its porosity when it is heated within such a temperature range as it does

(24) At lower temperatures, the existence of the defect positions of this type is well understood.[16]

(25) W. Jander, *Z. anorg. allgem. Chem.*, **192** (1930), 295.

not melt completely,[26] has been utilized widely in the ceramic industry. Of course, the formation of a liquid phase, owing to the low melting eutectics, is one of the causes of sintering; however, the phenomenon occurs also in pure solid state and it is especially remarkable when a solid reaction takes place. Hedvall[27] called the phenomenon as "Trockensinterung" and, indeed, "Trockensinterung" of metals has recently been developed into so-called powder metallurgy.[28]

For the use of refractories, which are exposed to high temperatures, it is desirable that the high melting substances are selected, and in the course of their manufacture, they should be sintered at relatively low temperatures without forming any liquid phase. Now magnesium oxide, which has a very high melting point and is well qualified as a basic refractory, sinters at a lower temperature than its melting point; and while it has been known that the existence of such oxides as Fe_2O_3 or Al_2O_3 is, probably owing to the formation of an addition compound, effective for its sintering, the author[29] has recently found further that the addition of a small quantity of TiO_2 is very effective in this connection. For instance, when the pressed bodies of the various mixtures of MaO and TiO_2 were ignited at 1400°, their porosities diminished as shown in Figure 4.[30]

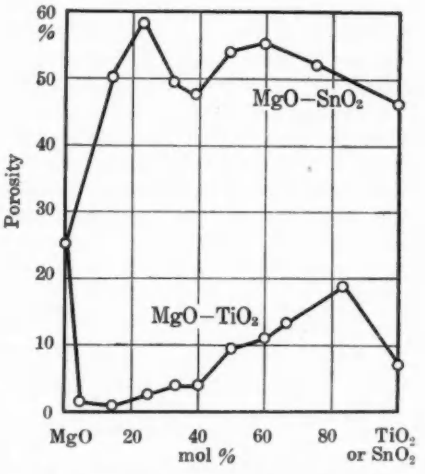

Fig. 4. Porosities of the ignition products at 1400° of the systems MgO-TiO_2 and MgO-SnO_2.[31]

In this system the sintering is particularly remarkable by the mixtures in which $2MgO \cdot TiO_2$ is formed. While MgO belongs to the cubic system, $2MgO \cdot TiO_2$ has also a cubic spinel structure; and it is easily expected that the spaces among the crystals become smaller when the particles of the same crystal system are packed most closely to each other than in the other cases. Fe_2O_3 and Al_2O_3, too, form with MgO addition compounds with the spinel structure.

However, the addition of SnO_2 (which belongs, as well as TiO_2, to the fourth group of the periodic system and also forms with MgO the

(26) While the meaning of sintering is not certain, it is defined here as above.
(27) J. A. Hedvall, *loc. cit.*, 81.
(28) *Cf.*, for instance, W. D. Jones, "Principles of Powder Metallurgy," London (1937); W. Seith, "Diffusion in Metallen," Berlin (1939).
(29) Y. Tanaka, *J. Soc. Chem. Ind. Japan*, **42** (1939), 387, 202B; 390, 204B; Y. Tanaka and T. Takagi, *J. Soc. Chem. Ind. Japan*, **42** (1939), 874, 405B.
(30) *J. Chem. Soc. Japan*, **60** (1939), 212.
(31) Let W be the weight of a porous solid substance, V be its total volume and s, its specific gravity, then the porosity, P, is calculated from

$$P = \frac{s - W/V}{s} \times 100\% \ .$$

spinel type compound, $2MgO \cdot SnO_2$) is not effective at all for the sintering of MgO; the porosities of this system at 1400° are also given in Figure 4.[32][33] Therefore, it is easily conceivable that sintering, due to the solid reaction, depends not only on the structure of the addition compound but also on the reaction mechanism.

As for the above two systems, the following discussions may be given. Namely, by the reaction between MgO and TiO_2, MgO migrates on the surface of TiO_2 and, as seen from Figure 3, the particles of MgO are deformed and their sizes decrease gradually. Therefore, the total body shrinks and, furthermore, it is considered that the crystal growth of MgO is accelerated by the stress due to its deformation; thus the body sinters by the reaction. On the other hand, by the reaction between MgO and SnO_2, the surface diffusion occurs but slightly and the reaction takes place chiefly in the neighbourhood of the contact points of the components, and especially, as shown in Figure 2, if it is assumed that the components exchange each other with nearly equal quantities,[34] the particle sizes of the two components are unchanged; therefore, the vacant spaces remain as before and no sintering should be observed. The reaction between MgO and Al_2O_3 belongs to the former case, and the body sinters actually.

The author would like to point out, further, that the existence or non-existence of the surface diffusion and the phenomenon of sintering may play an important rôle in manufacturing mixed catalysts.

Experiments on the Effect of Particle Size.

VII. The Reaction between Magnesium Oxide and Stannic Oxide. The effect of particle size of the components on the reaction between MgO and SnO_2, where no distinct surface diffusion has been considered to take place, was studied at first. With a mixture corresponding to the addition compound, $MgO:SnO_2=2:1$, the particle size of one of the components was kept constant, as 150 to 200 meshes to the inch, and that of the other component was changed.

Although it was difficult to obtain coarse particles from commercial preparations of MgO and SnO_2 (and of other oxides also) which were very fine powders, this was achieved by the following method: as the preparations were hardened moderately when they were kneaded with some water, dried and heated at 1200° to 1300°, they were crushed carefully and passed through different sieves. Although these particles consisted by no means of single crystals and were different in shape, they were assumed to be spherical, and their "mean radii" were estimated approximately as given in the second column of Table 2.

The amounts of free MgO and those of SnO_2, soluble in 4N HCl, of the reaction products at 1100° are given in Table 2. The reaction proceeded slowly within a half an hour and after 3 or 6 hours it seemed to have proceeded normally. The reacted amounts were calculated from the percentage of soluble SnO_2 based on the theoretical value of total SnO_2 though it contained, as it was stated in the third report,[8] some amorphous SnO_2.[35]

(32) *J. Chem. Soc. Japan*, **61** (1940), 1023.

(33) As the sintering of TiO_2 and SnO_2 themselves are different from each other, the comparison is not strict; however, the tendency is obvious.

(34) When the reaction proceeds by the ionic diffusion, this condition is satisfied.

(35) Since mixing of the components containing coarse particles can hardly be executed completely homogeneous, to calculate the reacted amount from free MgO will introduce much uncertainty. Ideally, a total analysis should be made with each reaction product.

Table 2. Effect of Particle Size on the Reaction between Magnesium Oxide and Stannic Oxide. $MgO:SnO_2=2:1$ ($SnO_2=65.14\%$), 1100°.

Particle size of MgO		Particle size of SnO_2	Free MgO	SnO_2 Soluble in 4N HCl	Free MgO	SnO_2 Soluble in 4N HCl	Free MgO	SnO_2 Soluble in 4N HCl
Meshes/inch	Mean radius (mm)	Meshes/inch	(%)	(%)	(%)	(%)	(%)	(%)
Reaction time (hrs.)			0.5		2		6	
32– 48	0.20	150–200	33.13	4.16	32.12	6.90	31.59	7.98
65–100	0.09	"	32.80	4.75	31.32	8.27	30.37	10.46
150–200	0.04_5	"	32.73	4.98	30.60	10.57	29.08	13.65
200–*	0.02_5	"	32.60	5.27	30.27	11.05	27.99	15.08
150–200	0.04_5	32– 48	33.86	2.60	33.53	3.52	32.48	5.38
"	"	65–100	33.33	3.93	31.77	8.79	30.81	10.02
"	"	200–*	32.46	5.68	29.96	11.13	27.68	16.70

* Pulverized with an agate motar as fine as possible.

As shown in Figure 5, the curves in which the reacted amounts are plotted against the reciprocals of the mean radii of MgO or SnO_2 particles at each reaction time turn out just as discussed in §1(*b*) of section III. However, the effect of the size of SnO_2 is a little greater than that of MgO which indicates that MgO migrates to some extent on the surface of SnO_2.

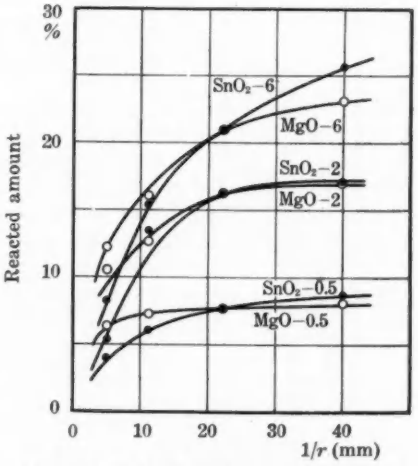

Fig. 5. Relations between the reacted amounts and the reciprocals of the mean radii of the components by the reaction between MgO and SnO_2 at 1100°.

SnO_2-2 means, for instance, the reacted amounts at two hours with varying the particle size of SnO_2.

VIII. The Reaction between Magnesium Oxide and Aluminium Oxide. As in the above experiment, with a mixture of $MgO:Al_2O_3=1:1$, the effect of particle size on the reaction between MgO and Al_2O_3 was studied at 1200°. The reacted amounts were expressed by the percentage of combined to total MgO, which was, in case of the mixtures containing coarse particles, determined by total analysis.

The results are given in Table 3, and the relation between the reacted amounts and the reciprocals of the particle sizes are shown in Figure 6. Contrary to the results of the reaction between MgO and SnO_2, the effect of the particle size of MgO is far greater than that of Al_2O_3. Namely, when the particle size of Al_2O_3 is constant, the reacted amounts are nearly proportional to the reciprocals of the mean radii of MgO particles, or to the surface area of MgO; while the effect of the size of Al_2O_3 is not so remarkable unless its size is not very coarse. This agrees with the discussion of §2 of section III.

Table 3. Effect of Particle Size on the Reaction between Magnesium Oxide and Aluminium Oxide. $MgO:Al_2O_3=1:1$ (MgO=28.34%), 1200°.

Particle size of MgO Meshes/inch	Particle size of Al_2O_3 Meshes/inch	Reacted amount (%)	
Reaction time (hrs.)		1	6
32– 48	150–200	4.30	5.19
65–100	"	8.29	10.59
150–200	"	17.78	24.45
200–*	"	26.60	38.99
150–200	32– 48	8.17	13.33
"	65–100	12.70	22.20
"	200–*	19.47	27.30

* Very fine.

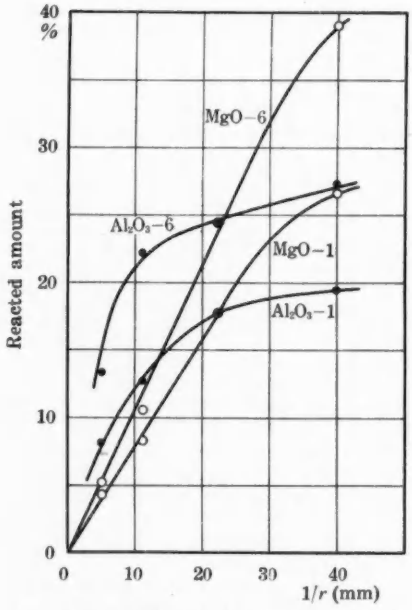

Fig. 6. Relations between the reacted amounts and the reciprocals of the mean radii of the components by the reaction between MgO and Al_2O_3 at 1200°.

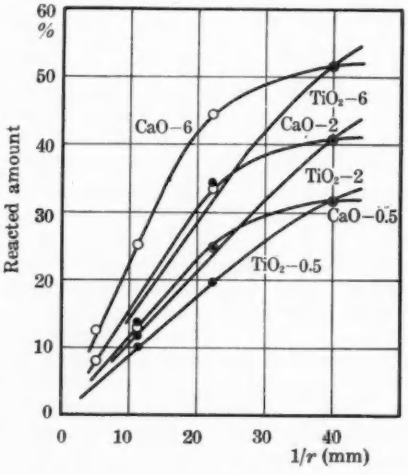

Fig. 7. Relations between the reacted amounts and the reciprocals of the mean radii of the components by the reaction between CaO and TiO_2 at 950°.

IX. The Reaction between Calcium Oxide and Titanium Oxide. The results of the experiment with a mixture of $CaO:TiO_2=1:1$ at 950° are shown in Table 4 and in Figure 7. The reacted amounts were calculated from the percentage of combined to total CaO.[36]

(36) As the combined CaO was calculated from free CaO, the existence of some uncertainty was unavoidable. Moreover, since one of the components was kept constantly to be very fine powders, smaller than 200 meshes to the inch, the results were not so clear.

Table 4. Effect of Particle Size on the Reaction between Calcium Oxide and Titanium Oxide. $CaO:TiO_2=1:1$ (CaO=41.24%), 950°.

Particle size of CaO Meshes/inch	Particle size of TiO_2 Meshes/inch	Reacted amount (%)		
Reaction time (hrs.)		0.5	2	6
32– 38	200–*	8.7	8.0	12.6
65–100	"	12.9	14.3	25.2
150–200	"	24.8	33.4	44.4
200–*	"	31.7	40.7	51.6
200–*	65–100	10.1	11.8	13.6
"	150–200	19.7	25.2	34.4

* Very fine.

Although the effect is not so distinct as in the reaction between MgO and Al_2O_3, it is obvious as far as that the effect of the particle size of TiO_2 is greater than that of CaO, and that a linear relationship between the reacted amounts and the reciprocals of the particle sizes holds approximately for the former. It seems that the inner diffusion takes place comparatively easily in this reaction.

Summary.

(1) The main characteristics of the solid reactions between the oxides, studied in the present investigations, have been summarized. These reactions can be classified into the following two types: (1) the reactions of the systems, MgO–TiO_2, CaO–TiO_2 and MgO–Al_2O_3, which have a rapid initial reaction period and a small energy of activation, and (2) those of the systems, MgO–SnO_2 and CaO–SnO_2, in which no rapid initial reaction and a large energy of activation are observed.

(2) The rapid initial reaction is probably due to the existence of a rapid surface diffusion, and when the reaction proceeds chiefly by the inner diffusion, no rapid initial part may be observed.

(3) The effect of the particle size of each of the components on these reactions has been discussed. In the reactions without distinct surface diffusion, the effect of the particle size of the component, of which total surface area is smaller, should be great, while that of the diffused component becomes remarkable when the sufrace diffusion takes place rapidly.

(4) For the three reactions, MgO–SnO_2, MgO–Al_2O_3 and CaO–TiO_2, the above discussions have been proved experimentally by changing the particle size of each of the components.

(5) Technical importance of the effect of particle size on solid reactions has been stated.

(6) Some further considerations on the diffusion mechanism have been given, and the difference in the energies of activation has been interpreted.

(7) Finally, the phenomenon of sintering due to solid reactions has been discussed. It is considered that the sintering occurs by the reactions in which a rapid surface diffusion takes place.

In conclusion, the author wishes to express his sincere thanks to Dr. R. Yoshimura for his interest, to Mr. K. Hirota for criticizing and discussing the problem willingly, and also to Dr. R. Negishi and to the other colleagues. He is also indebted to Messrs. S. Takasago and T. Sugawa for their assistances in the experiments.

Further the author takes this occasion to express his hearty gratitude to Prof. Y. Shibata of Tokyo Imperial University, to Prof. T. Marusawa, the former Director of the Central Laboratory, and to Dr. M. Sato, the present Director, for their keen interests and constant encouragement in carrying out the present series of investigations.

Department of Inorganic Chemistry, The Central Laboratory,
South Manchuria Railway Company, Dairen.

Hydrocarbons from Carbide (A) III.* Non-catalytic Polymerization under Ordinary Pressure. Carbon Dioxide-, Carbon Monoxide-, and Hydrogen Chloride-Calcium Carbide Systems.**

By Ryoji NEGISHI and Osamu KAMIIKE.

(Received January 12, 1942.)

In our first paper[1] of the present series, we have reported on the results of the orientation runs made with hydrogen and, with the informations gained therefrom, we have made a series of runs with carbon dioxide, water gas, and hydrogen chloride, singularly or with their mixtures, to increase further the yield of liquid products. Their results will be given in this paper. We shall reserve a fuller discussion on the results and on the mechanisms of the reaction in question for the third and final paper of this series of investigations on the non-catalytic polymerization under ordinary pressure.

I—Carbon Dioxide System.

We have chosen this system first, because we are reasonably certain that there will be no oil formation[2] from the gas itself which probably

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* This paper has been published by permission of Dr. M. Sato.

** The experimental details of these systems have been given in a series of papers published in Japanese in *J. Soc. Chem. Ind. Japan*, **44** (1941), 1028; ibid., **45** (1942), 133.

(1) R. Negishi and O. Kamiike, Paper (A) II, this Bulletin, **17** (1942), 118.

(2) F. Fischer, *Brennstoff-Chem.*, **10** (1929), 279. According to him, when acetylene is mixed with 10% CO_2, the yield of liquid products increases, but there is no reaction involving CO_2, except that only about 0.27% of it is transformed into CO and traces of water.

would not be the case with acetylene or with water gas, and we can ascribe the whole mechanism of the oil formation to nascent acetylene.

In this section of the paper, only those runs with carbon dioxide alone and its mixture with hydrogen will be dealt with, and the runs with hydrogen chloride will be given at the time the latter system is discussed.

Most of the runs were made at 340°C and some at higher temperatures only when the supplementary data were necessary. Experimental conditions are given in Table 3.* The apparatus, the procedure of run, and the materials used have already been given.[1] In this and the subsequent investigations of the series, however, "desorption," (so designated for want of a better term) has been effected as follows: after the reaction had been conducted for a given period of time, the reaction gas** was switched over from the saturator to the by-pass, and the dried gas was introduced into the reaction zone. The temperature of the furnace was then raised. When the temperature was raised above 400°C, the effect of desorption was evident, as shown by a large amount of condensation along the cooler parts of the reaction tube. When the amount of condensation became small, the temperature was lowered to the original point, and the gas was switched back to the saturator. This process was repeated as often as necessary, but usually two per run sufficed.

Table 1. Carbon Dioxide-Carbide System.

Exp. No.	I_L37	I_L40	I_L41	I_L57	I_L59	I_L60
React. Temp. (°C)	380–400	340–380	340–380	340	380	420
Gas	CO_2	CO_2+H_2	CO_2+H_2	CO_2	CO_2	CO_2
Saturation temp. °C	80	80	72	80.3	80.3	80.3
Ratio Gas to Water (partial Press.)	1 : 0.85	$CO_2:H_2:H_2O$ 2 : 1 : 2.67	$CO_2:H_2:H_2O$ 1 : 1 : 1	1 : 0.86	1 : 0.87	1 : 0.87
Time of Contact (sec.)	15.6	22.2	16.7	22.1	18.8	16.1
Liq. Prods. (g.)***	13.95	14.7	17.2	27.9	21.5	10.3
Water	10.9	13.0	3.8	9.0	29.4	18.8
Oil on Reacted (%) Carbide Acetylene	35.5	32.7	33.6	43.3	38.8	23.9
Oil on Reacted (%) Carbide Carbon	31.20	29.6	31.1	41.0	35.7	22.21
Carbon Balance	96.6	98.5	95.6	99.6	97.7	—
Wt. Balance	98.1	98.3	99.7	99.3	100.2	95.0

200 g. of carbide was used in every run.

Results and Discussion. Out of a large number of runs, only those which are sufficiently accurate to give either the total weight balance or the carbon balance more than 95% are shown in Table 3. The results of the first three runs are less comparable, because they are more or less explorative in nature, and the reaction temperatures have been varied over a wide range. Those of the last three runs are, however, quite

* The numbering of the Tables and Figures are consecutive throughout the whole series of papers, from (A) II to the final one.

** When a different gas, for example, H_2 or CO_2, was used to effect desorption, the reaction gas was shut off, and the dry gas in question was introduced from the by-pass.

*** Hydrocarbons.

comparative, and some interesting and suggestive results are possible from them. As has been the case with our first report,[1] the maximum yield of liquid products is again at 340°C* and at higher temperatures it diminishes. The ratio of liquid products to water seems to decrease with an increase of temperature, even when the extent to which the carbide has reacted is taken into consideration.

The percentage of the liquid products have been calculated on two different bases, namely, one on the reacted carbide acetylene and the other on the reacted carbide carbon. This sort of calculation has been performed, because we are really interested in the total amount of the liquid products which can be obtained from the carbide, or acetylene, (it is what becomes of the acetylene that is pertinent). There is also another reason for making this calculation. If the products are hydrogenated, the percentage of the liquid products will increase in proportion to the degree of hydrogenation, since the total weight of the liquid products is considered on the acetylene basis, while on the carbon basis, it will remain the same. Therefore, by comparing the two sets of percentages, we can obtain some idea as to the extent to which the products are hydrogenated and some information with regard to the mechanism of the reaction. If the two sets of values are the same, it means that there is no hydrogenation, or that there is no product of which H/C ratio is greater than that of acetylene; in other words, the reaction is simply

$$n\mathrm{C_2H_2} = (\mathrm{C_2H_2})_n \,.$$

It is obvious from the results of Table 3 that the yield, calculated on acetylene, is always larger than that on the carbon. It may mean several things: either the whole products contain slightly more hydrogen than that in acetylene molecule or the majority of the products has about the same H/C ratio as that of acetylene, but there is present a small quantity of a substance with a very much higher H/C ratio. The data are not sufficiently accurate nor copious to decide which of the two is most probable, but the results of the elementary analysis in Table 4 are suggestive. It is rather surprising that the products contain so much oxygen. If it is assumed that most of it is due to methyl alcohol, which has been identified, we get some interesting results, as illustrated by I_L 57. Let us take the trap condensates of which elementary analysis gives the following results:

$$\mathrm{C} = 74.98, \quad \mathrm{H} = 9.37, \quad 0 = 15.65, \quad \mathrm{H/C} = 0.1250.$$

Now, if we assume that all of this oxygen is due to methyl alcohol and make correction accordingly, the final H/C becomes 0.0853, while that of acetylene is 0.0833. The ratios of the percentages based on acetylene to those based on carbon are practically constant and greater than unity but slightly. From these facts we may assume reasonably that the majority of the products has a H/C ratio which is very nearly equal

* This seemed to be the case in the whole series of runs made under the ordinary pressure with the gases which are not themselves capable of polymerizing into liquid products. This point will become more clear when the results with other gases, especially acetylene, are reported later in this Bulletin.

to that of acetylene, but a small amount of substance with a higher ratio is also present. The main reaction of the nascent acetylene molecules, therefore, seems to be

$$n C_2H_2 = (C_2H_2)_n ,$$

whether H_2 (and CO_2) is present in the system or not.

Tabele 4. Gas Analysis (Carbon Dioxide-Carbide System).

Gas	I_L37 (%)	I_L40 (%)	I_L41 (%)	I_L57 (%)	I_L59 (%)	I_L60 (%)
CO_2	72.8	33.5	30.5	56.6	64.6	72.8
C_2H_2	10.5	17.4	8.4	18.8	22.2	12.1
C_2H_4	0.9	0.6	0.6	0.2	0.4	0.4
C_nH_{2n}	0.0	—	0.0	0.1	0.7	0.6
O_2	0.6	0.8	0.9	0.4	0.6	0.2
CO	0.6	0.6	0.6	0.3	0.8	0.4
H_2	7.4	41.2	50.4	18.3	5.8	8.3
CH_4	3.5	2.2	1.9	2.2	2.4	3.3
N_2	4.0	3.5	3.9	4.0	2.8	2.4

The first striking thing about the results of elementary analysis in Table 4 is, as has been mentioned above, the high content of oxygen in the products, especially in the trap. Just what sort of oxygen we have here is at present difficult to say, but some evidence indicates that it is predominantly alcoholic. When the last three results in Table 4 are compared, it is interesting and may be of significance, that, both in the trap and condenser, the carbon content increases, while H/C ratio and the oxygen content decrease, respectively, with increasing temperature. When the analysis of the liquid products becomes more complete, we may be able to give a proper interpretation of the results.

In Table 5 the results of gas analysis are given. They should be considered qualitatively rather than quantitatively, since they do not represent the real compositions of the effluent reaction gas, owing to the fact that part of the effluent gas during desorption is invariably mixed with the effluent reaction gas. As for example, a high content of hyrogen in I_L 57 is due, undoubtedly, to the circumstance that desorption has been effected with hydrogen. Even with this limitation, a general trend in the change of the composition with temperature is as has been found in Paper (A) II[1] when the last three runs are compared.

There may remain some doubt as to the real significance of desorption, as defined in this paper, and in order to remove it I_L60 has been made. It became clearer from the results of this paper and those of a number of unpublished data that most of the liquid products were desorbed at near 420°C. If the apparent increase in the yield at the time of desorption is due rather to the increase in the oil formation at higher temperatures, the total yield should be higher for the reaction made at about 420°C than at lower temperatures. The data in Table 3 clearly indicate that the increase in the yield is due to a more efficient liquid formation

at lower temperatures plus the effect of desorption, and not due to that of higher reaction temperature.

Table 5. Elementary Analysis (Carbon Dioxide System).

Element	I_L37 Combined	I_L40 Trap	I_L40 Cond.	I_L41 Trap	I_L41 Cond.	I_L57 Trap	I_L57 Cond.	I_L59 Trap	I_L59 Cond.	I_L60 Trap	I_L60 Cond.
C(%) ..	81.23	78.66	84.92	83.02	84.02	74.62	83.19	77.43	85.75	80.56	86.59
H " ..	8.62	9.93	8.53	10.10	8.46	9.96	8.76	10.24	8.60	9.76	8.49
C " ..	10.15	11.41	6.35	6.88	7.52	15.42	8.05	12.32	5.65	9.68	4.92

Finally, the results of the present work indicate that the only reaction in which carbon dioxide is involved is that of the formation of carbonate, in agreement with the observations of Fischer[2]. Run I_L40 illustrates this point effectively. In this calculation the following have been assumed: (a) only acetylene forms the liquid, higher polymers, other gases (olefines and saturated), and free carbon; (b) the originally contained carbonate does not take part in any reaction. The results of calculation are gratifying.

Source of Carbon	Introduced (g.)	Found: Free Gas (g.)	Decomp. +High Polym. (g.)	Carbonate (g.)	Liquid (g.)	Other Gases (g.)	Unreacted (g.)	Sum (g.)	Balance
C_2H_2	62.92	13.84	12.64	——	12.36	1.49	21.28	61.61	1.31
CO_2	30.10	13.30	——	16.76	——	——	——	30.06	0.04
Carbonate ..	1.17	——	——	1.17	——	——	——	1.17	(0.0)

II—Carbon Monoxide System.

In this system we have investigated the effect of a carrier gas which is itself capable of forming liquid products. From the studies of the hydrogen and of the carbon dioxide systems, we have obtained some indications that the main reaction of nascent acetylene is not influenced by carrier gases. It has been hoped, therefore, that it may be possible to effect a typical Fischer-Tropsch reaction (in the absence of a catalyst for the reaction) in parallel with the main reaction of the carbide.

The experimental results are given in Table 6 in which I_L62, of which weight balance deviates by more than the usual limit, $\pm 5\%$, has been included for the sake of comparison. It must be added here that we have had a great deal of experimental difficulty with this system. Quite frequently the reaction tube cracked without any warning, and although we had made quite a number of runs with CO alone and with its mixtures, only the two, given in the Table, appeared sufficiently quantitative. It may also be mentioned that for every run that appears in the Table, at least five runs have been made that are not sufficiently quantitative and are, therefore, not shown in the Table. Recourse to them, however, will be freely made in our discussion.

Table 6. Carbon Monoxide-Carbide System. Hydrogen Chloride-Carbide System.

Exp. No.	I_L44	I_L50	I_L64	I_L65	I_L62
Reaction Temp.(°C)	340	340	340	340	380
Gas	CO	$CO+H_2$	CO_2+HCl	CO_2+HCl	H_2+HCl
Saturation Temp.(°C)	80.1	72.5	79.3	80	90.5
Ratio Gas to Water (Partial Press.)	$CO:H_2O$ 1:0.85	$CO:H_2:H_2O$ 2:4:3	$HCl:CO_2:H_2O$ 0.1:409:347	$CO_2:H_2O$* 1:0.86	$HCl:H_2:H_2O$ 174:311:275
Time of Contact (sec.)	19.0	29.3	21.4	26.7	23.9
Liq. Prods. (g.)	6.4	5.2	23.7	19.2	7.7
Water (g.)	3.0	0.4	17.2	13.6	27.15**
Oil on Reacted (%) Carbide Acetylene.	10.3	22.0	39.9	38.9	31.6
Oil on Reacted (%) Carbon (Carbide)	10.2	20.3	33.2	35.1	27.6
Carbon Balance	102.0	98.3	97.4	96.5	—
Weight Balance	100.6	100.5	98.3	96.1	81

200 g. of calcium carbide grains was used in every run.
* Traces of HCl.
** H_2O+23.9% HCl.

Before we made the experiments, we had hoped, according to our thermodynamic calculations[3], that we might obtain a larger total yield of liquid products by using water gas as a carrier gas, but our experimental results seemed to point otherwise. In fact, they indicated that the gas not only failed to form any liquid,* but had actually decreased** the yield, as shown in Table 6. The small yield might have been due to the fact that in these runs no desorption has been effected, but this can account only for a small part, since it is shown that the effect is appreciable only when CO_2 is involved as in I_L64. We are at present unable to offer a comforting explanation for the harmful effect of carbon monoxide or water gas on the direct synthesis of hydrocarbon liquids from the carbide.

The results of gas analysis in Table 7 should be considered rather qualitatively than quantitatively for the same reasons given in connection with CO_2 system. The results of semi-quantitative calculation, based on the gas analyses of I_L44 and I_L50, showed that part of the original CO had reacted to form CO_2 (eventually it produced calcium carbonate) and methane, but no liquid products.

(3) R. Negishi, O. Kimura, and O. Kamiike, *Rev. Phys. Chem., Japan*, **15** (1941), 31, Paper (A) I.

* I_L47 was made to see whether the carbide had any effect on a dry $CO+H_2$ mixture of 1:2 proportion or not. The temperature was varied from 150°C to 450°C, but there was no liquid formation; moreover, there was but slight reaction of any sort, as indicated by the negligible change in the weight of the carbide before and after the reaction (from 200 to 200.5 g.) and by the results of gas analysis (gas at 300°C) shown in Table 7. The original composition was about the same as that of I_L50.

** For I_L52, made under the same conditions as those of I_L50, the yield of liquid was 20.0%.

Table 7. Gas Analysis.

Gas	I_L44 Reacted (%)	I_L44 Introd. (%)	I_L50 Reacted (%)	I_L50 Introd. (%)	I_L64 (%)	I_L65 (%)	I_L62 (%)	I_L47 (%)
CO_2	0.67	0.9	0.47	—	71.26	76.7	2.48	1.8
C_2H_2	8.75	—	6.20	—	15.68	16.9	6.77	1.0
C_2H_4	0.37	—	0.43	—	0.58	0.4	0.64	0.4
C_nH_{2n}	0.30	—	0.37	—	0.37	0.2	0.50	0.0
O_2	0.51	—	0.80	—	0.32	0.4	0.94	1.4
CO	71.34	99.2	23.88	31.6	0.48	0.2	0.54	28.2
H_2	9.28	—	60.54	61.9	6.90	2.3	80.89	58.8
CH_4	3.75	—	1.70	—	2.33	1.2	4.74	2.0
N_2	5.15	—	6.00	6.3	2.58	2.4	2.34	6.4

III—Hydrogen Chloride System.

Hydrogen chloride has been used to investigate the effect on the yield of the destruction of the basic substances produced in the reaction and the catalytic effect—if any—of the acid.

The effect of hydrogen chloride vapors seemed but slight. Although there was some difference in the physical appearance of the liquid products in runs I_L62 and I_L64, it might very well be accounted for by other effect than that of the acid concentration.* We hesitate to make a definite conclusion as to the effect on the yield of liquid products of the acid and also of the carbonate, but the results of Tables 8 and 9 are suggestive.

Table 8. Carbonate Carbon in Residue.

Exp. No.	Wt of Residue (g.)	CO_3 Carbon in Residue (g.)	CO_3 Carbon on React. CaC_2 Carbon (%)
I_L64	288.1	27.46	47.5
I_L62	277.4	2.67	10.4
I_L65	283.3	23.43	47.5
I_L57	389.9	25.91	46.3

Table 9. Effect of Acid on Liquid Yield (at 340°C).

Exp. No.	HCl Conc. Wt. (%) Average	Vap. Press. mm Hg HCl	Vap. Press. mm Hg H_2O	Vap. Press. mm Hg CO_2	Liquid Carbon on React. Carbide Carbon (%)
I_L62*	26	174	267	324*	28
I_L64	3.5	0.1	347	409	33.2
I_L65	0.58	Trace	350	410	35.1
I_L57	0.0	0.0	350	410	41.0

* At 380°C; instead of CO_2, H_2 was used.

* The concentration of HCl in the saturated vapor was computed from the partial vapor values given in Int. Crit. Tables, Vol. III (1928), 301. Its concentration in the vapor phase was expressed in mm Hg and that in the liquid by weight percent, determined by titration with Na_2CO_3.

In Table 10 the results of elementary analysis of the liquid products are given. It seems that the products formed in the presence of CO contain less oxygen while those formed in the presence of the acid contain larger amounts than those with carbon dioxide. A proper explanation also awaits for this peculiar effect, if real.

Table 10. Elementary Analysis.

Element	I_L44		I_L50	I_L64		I_L65		I_L62	
	Trap	Cond.	Combined	Trap	Cond.	Trap	Cond.	Trap	Cond.
C(%)	82.02	84.60	85.20	74.29	79.79	67.70	84.96	——	81.63
H "	9.71	8.69	8.76	10.10	8.78	10.48	8.85	——	8.20
O "	8.27	6.71	6.04	15.61	11.43	21.82	6.19	——	10.17

Summary.

The effects on the synthesis of hydrocarbon liquids directly from calcium carbide, in the temperature range of 340 to 420°C, of carbon dioxide, carbon monoxide, hydrogen choride, and their mixtures have been studied. The present results are in general agreement with those of the hydrogen system, and it has been found that the main reaction of the nascent acetylene molecules is but slightly affected by the carrier gases.

In the carbon dioxide system the yield of liquid products has been found as high as 43% of the total reacted acetylene. The only reaction in which carbon dioxide takes part is the formation of calcium carbonate. The presence of hydrogen seems to have no effect on the character of the liquid products.

It has been shown that while carbon dioxide has favourable, carbon monoxide has unfavourable effects, and hydrogen chloride has none at all, or but slight, on the liquid yield.

In the presence of the carbide and its reaction products, carbon monoxide with hydrogen does not effect a Fischer-Tropsch synthesis; however, it reacts to produce some carbon dioxide and methane.

The Central Laboratory,
South Manchuria Railway Company, Dairen.

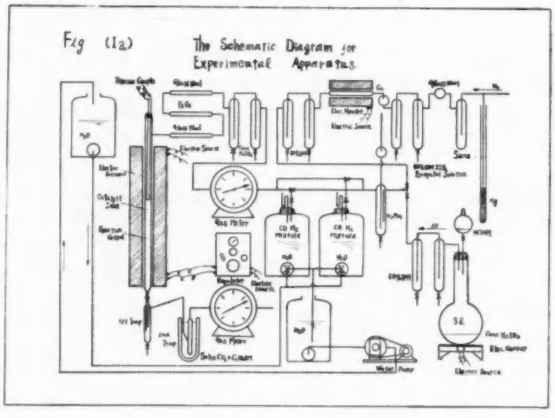
Physico-Chemical Investigations on Catalytic Mechanism. (V). On the Fischer-Tropsch Synthesis of Hydrocarbons. (Experimental Series II*).[1]

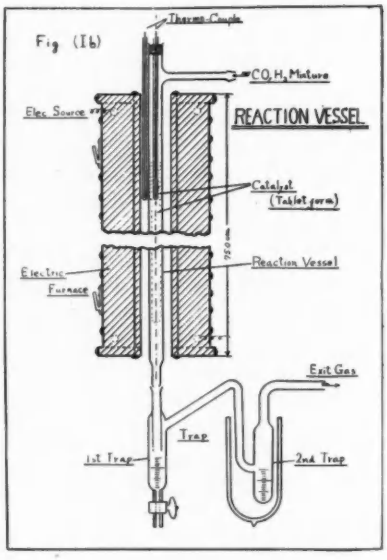
By Senzo HAMAI, Shiro HAYASHI and Kiyoshi SHIMAMURA.

(Received January 14, 1942.)

In a previous paper[1] we described the experimental apparatus by which a series of investigations concerning the catalytic mechanism has been studied. In this paper we shall attempt to report some of our further experimental results obtained from similar series of the experiments, made by using other set of apparatus; hereafter, for our convenience we shall call this series II.

Experimental Apparatus. The principal features of the apparatus are practically the same as before, except a few details of the reaction vessel. They are shown in Fig. 1 a and Fig. 1 b.





The main feature of the reaction vessel is, as shown in Fig. 1 b, a tube of all terex glass of which dimension is 1.4 cm. in diameter and

* Most of the results given in this paper were obtained and completed in 1939–1940, but the publication of them has been with-held.

(1) S. Hamai, S. Hayashi, K. Shimamura and H. Igarashi, *Bull. Chem. Soc. Japan*, **17** (1942), 166 (Report IV).

94 cm. in length, and the thermocouple well is well inserted to the tube as far as the middle part of the catalyst zone so as to enable us to record even a slight variation of temperature during a run.

Electric furnace was controlled by means of an accurate regulator of potentiometric type.

Catalyst. The catalysts which we have employed are of Co, of Fe, and of Co–Fe types with various promoters and Kieselguhr.

In this series of experiments we used mainly the catalysts shown in Tables 1–3 (Co type), and they were prepared by the precipitation method from cobalt nitrate with potassium carbonate (2N) with an adequate

Table 1.

Effects of Promoters (CeO_2) on the Gas Contraction Reaction Temperature 200°C.

Exp. No.	Catalyst No.	Catalyst Composition (%) Co+CeO_2+Kieselguhr			Average Gas Contraction (%)
F_{30}(A–G)	XII_1–1	100	5	100	51
F_{31}(A–G)	XII_2–1	100	10	100	54
F_{32}(A–E)	XII_4–1	100	20	100	35
F_{33}(A–D)	XII_5–1	100	30	100	24
F_{36}(A–D)	XII_3–1	100	15	100	56
F_{35}(A–D)	XII_8–1	100	48	100	17

Table 2.

Effects of Promoters (ThO_2) on the Gas Contraction Reaction Temperature 225°C.

Exp. No.	Catalyst No.	Catalyst Composition (%) Co+ThO_2+Kieselguhr			Average Gas Contraction (%)
F_4	1_1–1	100	15	100	40
F_5	1_2–1	100	20	100	70
F_6	1_3–1	100	30	100	70
F_9	1_5–1	100	10	100	6
F_{12}	1_5–1	100	10	100	5
F_{13}	1_6–1	100	48	100	60

Table 3a.

Effect of ThO_2 on the Gas Contraction Reaction Temperature 200°C.

Exp. No.	Catalyst No.	Catalyst Composition (%) Co+CeO_2+ThO_2+Kiesel.				Average Gas Contraction (%)
F_{30}(A–D)	XII_1–1	100	5	—	100	51
F_{37}(A–D)	XII_7–1	100	5	5	100	35
F_{40}(A–G)	XII_{11}–1	100	15	15	100	34
F_{36}(A–D)	XII_3–1	100	15	—	100	56

Table 3b.

Effect of Cu on the Gas Contraction Reaction
Temperature 200°C.

Exp. No.	Catalyst No.	Catalyst Composition (%) Co+CeO_2+Cu+Kiesel.				Average Gas Contraction (%)
F_{30}(A–D)	XII_1–1	100	5	—	100	51
F_{38}(A–H)	XII_6–1	100	5	5	100	25

mixing of various promoters and Kieselguhr as a carrier, and were made into small tablet forms. (For a more detailed description for the preparation of the catalyst, see our report IV[1]).

Preparation of Gases involved in the Reactions. Hydrogen and carbon monoxide were prepared and purified in the same way as already described[1].

Experimental Procedure. As described previously in our report IV, the main features of experimental procedure are the same except that they were carried out in various different conditions.

The reaction products were collected in two separate portions—similar to those of Series I and subjected to the determinations of physicochemical properties.

The effluent gas was analyzed, using a modified form of Orsat Gas Analysis Apparatus for their constituents.

Experimental Results. In the present paper, we concern ourselves especially with different catalysts and their various influences on their activities and attempt to correlate with our theory of Fischer-Tropsch synthesis. Some of the illustrative results are tabulated as follows:

Table 1 and 2 show the influences of CeO_2[2][3] and ThO_2[3][4][5] in various percentages, and the characteristic behaviours of each catalyst are illustrated in Fig. 1 and 2. As seen in these graphs, it is more or less recognizable that the influences of CeO_2 and ThO_2 are not similar but quite distinct; namely in the case of CeO_2, the gas contraction percentage is higher with about 15–10% of this promotor, while if it exceeds 15% such as 20% or over, the gas contraction decreases distinctly. In the case of ThO_2, the gas contraction percentage is higher with about 20–30% of the oxide and below this it is not so favorable with regard to its activity, and one of the interesting points is that the relatively high percentage of ThO_2 content does not influence the activity as much as that of the relatively low one. However, an evenmore interesting point is that if the points of the maximum activity in both cases are traced and the contents of ThO_2 and CeO_2 are expressed respectively in the moral

(2) S. Kodama, *J. Soc. Chem. Ind. Japan*, (Suppl.) **33**, (1930) 202b.
(3) F. Fischer and H. Koch, *Brenn-chem.*, **13** (1932), 61.
(4) S. Tsutsumi, *J. Chem. Soc. Japan*, **59** (1938), 1412.
(5) S. Tsutsumi, *J. Chem. Soc. Japan*, **57** (1936), 685.

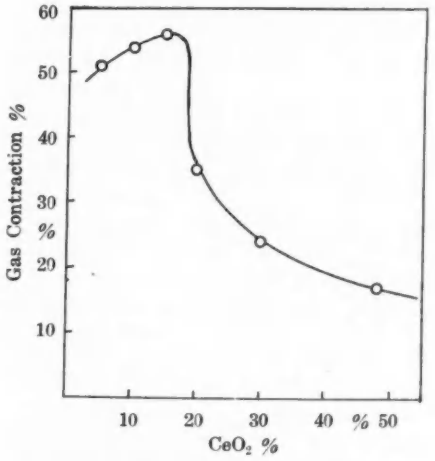


Fig. 1. Effect of CeO_2 % on The Gas Contraction %.
(Relatively High Yield of oil and Less Yield of CH_4)

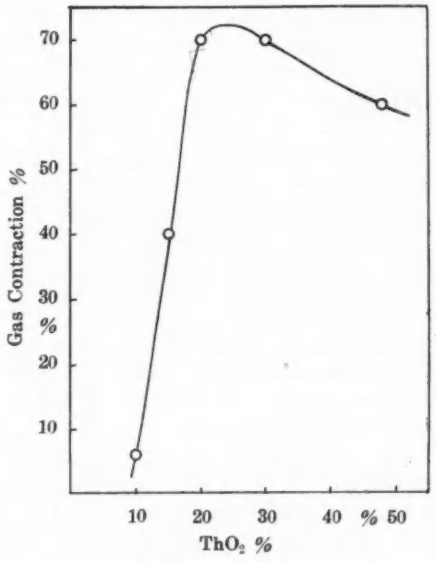


Fig. 2. Effect of ThO_2 on The Gas Contraction %.
(Relatively High yield of CH_4)

ratio(*) instead of the usual weight percentages, strange as they seem, they happen to be about the same, namely $Co:ThO_2=1:0.0513$ (23~25%), $Co:CeO_2=1:0.0513$ (15%), [$Co:ThO_2$, $1:0.0557$ (25%)]. These observed facts may be considered to be rather important from the stand point that in connection with the action of promoters, such as ThO_2 or CeO_2, the active centers to which the molecules of the promoters are distributed, are existing in such a manner as they seem to give the definite ratio. The interpretation of these phenomena may be very suggestive in regards to the theory of the promoter action, although such argument should not be put forward too far. At any rate, these facts, may possibly give a consequence fruitful in establishing the theory of promoter action.

Some investigators[3][6] have stated that the activity fell to zero when ThO_2 content was as high as 48%; but in our case the gas contraction percentage has been found to be as high as 60% with the same composition and it showed an activity almost as good as those of 20 and of 30%. These contradictory evidences show clearly that, as far as the catalytic activity is concerned, such a statement as cited in[3][6] does not have so much significance unless such facts are found absolutely reproduceable. This in turn implies that the investigation of catalytic mechanism, especially the catalytic activity, cannot be so easily discussed, even though the ex-

(*) Chemical properties are usually more closely connected with the molal ratio and better to be expressed in terms of molal properties of the system.

(6) S. Tsuneoka, "Synthetic Liquid Fuel" p. 65, (in Japanese).

perimental facts themselves might not be denied. But from these facts not only a clear-cut conclusion cannot be so easily drawn nor should be hastely deduced. Such experimental results themselves only tell a story of one side but not of general. Therefore, we can safely state that such evidence as the gas contraction percentage has true significance only for a definite reproducible condition.

The other interesting point is that, in the series of the catalysts containing CeO_2, a relatively high yield of oil and low yield of CH_4 are found even at the initial stage[7] of the run; while in the case of ThO_2, a relatively high yield of CH_4 and low yield of oil.

Table 3 shows some of the influences of ThO_2 as found on the average gas contraction and the effects of Cu.[8][3] As seen in Table 3, when CeO_2 percentage is relatively low, the addition of ThO_2 is found to lower the activity; while if CeO_2 is as high as 15%, the addition of 15% ThO_2 does not much improve the gas contraction, but it remains practically the same; so that the addition of ThO_2 does not seem to improve the activity as much as expected.

As regards the oil formation, it was found that in F_{36}(A–D), in which the contraction percentage was 56%, the yield of oil was approximately estimated to be 121.3 c.c./M^3.

Some of the typical gas analysis data are tabulated as follows:

Table 4.

Gas Analysis Dat

Exp. No.	F_{30}–A	F_{30}–B	F_{29}–C	F_{29}–D	F_{31}–G	F_{32}–E
CO_2	12.8	0.3	0.0	0.5	1.4	0.3
C_2H_2	0.0	0.0	0.0	0.0	0.0	0.0
C_2H_4	0.5	0.2	0.3	0.5	1.4	0.4
C_nH_{2n}	0.0	0.0	0.0	0.0	0.0	0.0
O_2	0.4	0.4	0.3	0.3	0.3	0.4
CO	6.1	31.8	31.5	31.6	29.4	31.5
H_2	39.8	65.2	66.0	65.4	66.1	65.3
CH_4	37.1*	0.0	0.0	0.0	0.0	0.0
C_2H_6	1.4	0.0	0.0	0.0	0.0	0.0
N_2	1.9	2.1	1.9	1.7	1.4	2.1

* Initial Stage.

(7) See: S. Hamai, *Bull. Chem. Soc. Japan*, **16** (1941), 213; Report IV, S. Hamai, S. Hayashi, K. Shimamura and H. Igarashi, *Bull. Chem. Soc. Japan*, **17** (1942), 166; E. F. G. Herington and L. A. Woodward, *Trans. Faraday Soc.*, **35** (1935), 958; *Brenn.-Chem.*, **20** (1939), 319.

(8) (a) F. Fischer, *Brenn.-Chem.*, **11** (1930), 489.
(b) K. Fujimura, *J. Chem. Ind. Japan*, **35** (1932), 532.
(c) S. Tsutsumi, *Report of the Fuel Research Institute, Japan*, **31** (1935).
(d) S. Tsuneoka and Y. Murata, *J. Chem. Ind. Japan*, **41** (1938), 95.
(e) F. Fischer and K. Meyer, *Brenn.-Chem.*, **12** (1931), 225.

Table 4.—(*Continued*)

Gas Analysis Date

Exp. No.	F_{33}–D	F_{35}–D	F_{36}–A	F_{36}–B	F_{36}–C	F_{36}–D
CO_2	0.5	0.2	3.5	0.9	0.3	1.4
C_2H_2	0.0	0.0	0.0	0.0	0.0	0.0
C_2H_4	0.3	0.4	0.9	0.5	0.6	0.7
C_nH_{2n}	0.0	0.0	0.0	0.0	0.0	0.0
O_2	0.2	0.3	0.6	0.3	0.3	0.4
CO	32.5	30.1	16.0	23.3	30.0	30.5
H_2	64.8	67.5	56.8	66.6	67.0	64.9
CH_4	0.0	0.0	19.6*	6.5*	0.0	0.0
C_2H_6	0.0	0.0	0.0	0.0	0.0	0.0
N_2	1.7	1.5	2.6	1.9	1.8	2.1

Table 5.

Gas Analysis Data

Exp. No.	F_4	F_5	F_6	F_9	F_{10}	F_{12}	F_{13}
CO_2	1.0	8.0	0.7	0.2	0.0	0.4	8.5
C_2H_2	0.3	0.3	0.2	0.4	0.0	0.3	0.7
C_2H_4	0.2	0.4.	0.2	0.0	0.5	0.2	0.0
C_nH_{2n}	0.5	0.3	0.0	0.0	0.3	0.0	0.0
O_2	0.4	0.3	0.3	0.4	0.4	0.3	0.4
CO	27.1	16.7	26.3	31.7	30.9	30.2	0.4
H_2	68.4	59.0	70.8	65.5	66.3	67.3	46.0
CH_4	0.0	12.8*	0.0	0.0	0.0	0.0	41.2*
C_2H_6	0.0	0.9	0.0	0.0	0.0	0.0	1.1
N_2	2.1	1.3	1.5	1.7	1.7	1.3	1.6

* Initial Stage.

As seen in these tables, CH_4 formation was observed at the initial stage[7] (F_{30}–A), F_{36}(A–B). In the case of F_{13} where ThO_2 content was 48%, the relatively high gas contraction percentage might be due to this abnormally high yield of CH_4.

As regards the influence of Cu on the activity of F_{30}(A–D) and F_{38}(A–H), it might be stated that, as far as these series of experiments are concerned, the addition of Cu seemed to lower the activity as evidenced by the average gas contraction. However, we must be cautious about drawing a general conclusion.

Thus far, we have shown some of typical results which indicate the various influences on the catalytic activity as caused by various amounts of promoters such as CeO_2, ThO_2 and Cu, along with the gas analysis data.

In Table 6 we have shown some of the physical and chemical properties of 1st and 2nd trap oils for the respective experiments.

Table 6.

Exp. No.	Reaction Temp. (°C)	Catalyst No.	Catalyst Comp.	Pretreatment hrs. °C	Physico-Chem. Properties: Ref. Ind.	Sp. Gr.	App. M. W.	Elem. Anal. C %	Elem. Anal. H %
F_4 1st trap oil	225	I_1–1	100 15 100	2 400 5 350	$1.4350^{25°}$	$0.7747^{20°}$	169	85.32	14.75
F_4 2nd trap oil	,,	,,	,, ,, ,,	,,	—	$0.7286^{20°}$	113	85.92	14.83
F_4 Wax	,,	,,	,, ,, ,,	,,	$1.4340^{65°}$ m.p. (58.6°–64.4°)	—	328	84.87	15.19
F_5 1st trap oil	225	I_2–1	100 20 100	2 400 5 350	$1.4211^{20°}$	$0.754^{20°}$	144	84.98	15.04
F_5 2nd trap oil	,,	,,	,, ,, ,,	,,	—	$0.6622^{0°}$	85	85.18	15.44
F_{30}(A–D) 1st trap oil	200	XII_{11}–1	100 5 100	5 400 5 350	$1.4319^{20°}$	$0.754^{25°}$	154	85.41	15.05
F_{30}(A–D) 2nd trap oil	,,	,,	,, ,, ,,	,,	$1.4090^{20°}$	—	102	84.45	15.55
F_{31}(A–G) 1st trap oil	200	XII_2–1	100 10 100	5 400 5 350	$1.4239^{20°}$	$0.746^{25°}$	149	84.87	14.84
F_{31}(A–G) 2nd trap oil	,,	,,	,, ,, ,,	,,	—	$0.7072^{5°}$	—	84.74	14.87
F_{32}(A–E) 1st trap oil	200	XII_4–1	100 20 100	5 400 5 375	$1.4317^{20°}$	$0.762^{25°}$	167	85.05	14.50
F_{32}(A–E) 2nd trap oil	,,	,,	,, ,, ,,	,,	—	—	—	—	—
F_{33}(A–D) 1st trap oil	200	XII_5–1	100 30 100	5 400 5 375	$1.4320^{20°}$	$0.765^{25°}$	166	84.53	14.97
F_{33}(A–D) 2nd trap oil	,,	,,	,, ,, ,,	,,	—	—	—	—	—
F_{35}(A–D) 1st trap oil	200	XII_8–1	100 48 100	5 400 5 375	$1.4297^{20°}$	—	—	84.50	15.16
F_{36}(A–D) 1st trap oil	200	XII_3–1	100 15 100	5 400 5 375	$1.4229^{20°}$	$0.745^{25°}$	143	85.56	15.00
F_{36}(A–D) 2nd trap oil	,,	,,	,, ,, ,,	,,	$1.4030^{22°}$	$0.668^{25°}$	90	84.19	15.51
F_{37}(A–D) 1st trap oil	200	XII_7–1	100 5 100 +5% ThO_2	5 400 5 375	—	—	—	—	—
F_{37}(A–D) 2nd trap oil	,,	,,	,,	,,	—	—	—	—	—
F_{38}(A–H) 1st trap oil	200	XII_6–1	100 5 100 +5% Cu	5 400 5 375	$1.4313^{20°}$	—	—	84.71	15.25

Table 6.—(*Concluded*)

Exp. No.	Reaction Temp. (°C)	Catalyst No.	Catalyst Comp. $CO+ThO_2+$ Kieselguhr	Pretreatment hrs. °C	Physico-Chem. Properties: Ref. Ind.	Sp. Gr.	App. M. W.	Elem. Anal. C %	H %
F_{38}(A–H) 2nd trap oil	,,	,,	,,	,,	$1.3980^{31°}$	$0.685^{20°}$	85	84.24	15.62
F_{40}(A–G) 1st trap oil	200	XII_{11}–1	100 15 100 +15% ThO_2	5 400 5 375	$1.4319^{20°}$	$0.766^{20°}$	153	85.69	14.42
F_{40}(A–G) 2nd trap oil	,,	,,	,,	,,	$1.4071^{20°}$	$0.702^{20°}$	90	85.08	15.23

Fifth Column; Indicates heat treatment prior to H_2 reduction and temperatures of H_2 reduction, respectively, in the order as written from the top.

Refractive index was determined by using Pulfrich refractometer, and the apparent molecular weights were determined by means of the freezing-point lowering method. The specific gravity was measured by using an ordinary pycnometer whose size was conveniently made as suitable to its respective amount of specimen.

Summary.

(1) Experimental apparatus for studying the catalytic mechanism for the Fischer-Tropsch synthesis with various different types of catalysts has been described and discussed (Series II).

(2) Influences of the CeO_2 content on the cobalt type catalyst as well as ThO_2 content along with the effect of Cu on the catalytic activity, as estimated by the average gas contraction, have been investigated.

(3) Typical gas analysis data for the effluent gas for each of these runs have been tabulated.

(4) Some of the physico-chemical properties of the reaction products have been determined and tabulated.

In conclusion, the authors take this occasion to express their sincere thanks to Dr. T. Marusawa, former Director of the Institute, and Dr. M. Sato, Director of the Institute, for their interests and encouragement during these series of investigations and also for the permission of the publication and we thank Messrs. Kuwabara, Igarashi, Fujiwara and Konoha who have assisted us willingly in the experimental part of this investigation.

The Central Laboratory,
South Manchuria Railway Company, Dairen.

Studies on the Adsorption at the Solid—Liquid Interface. III. Note on the Polar and Non-polar Adsorption.

By Hideo AKAMATU.

(Received February 21, 1942.)

On the Dielectric Theory of the Adsorption. Some relations between the adsorption and the dielectric nature of substances have already been known. It is about twenty years since the electrostatic theory concerning the force of the adsorption of gases or vapours has been proposed, and, since then, the theory has also been applied to the adsorption from the solution by many investigators.

According to the electrostatic theory[1] of the adsorption of vapour, the vapour molecules polarize the lattice of the adsorbent, and the certain molecules, which are near the surface of the adsorbent, is bound by the image force of itself in the lattice. In this case, the field induced by the adsorbent is not considered in general. In the case of the interface between the liquid and the solid, however, the potential difference between those two phases will vary widely as it depends on the dielectric structures of them. By the adsorption from the solution, moreover, the solvent molecules will be adsorbed, with the solute molecules at the same time, and therefore the amount of the adsorption will be given from the difference of these two amounts. In the dilute solution, with regard to a certain solute, the adsorption will increase, as less the adsorption of the solvent molecules is. Considering the electrostatic theory, the adsorption of the solvent molecules will be associated with their dipole moments. The adsorption will decrease, as greater the dipole moment of the solvent is. The adsorption of a certain solute are affected by the polarity of the solvent, and such phenomena were investigated by Nekrassow,[2] Heymann and Boye,[3] and Sata.[4] On the other hand, the solute will be more adsorbed from a certain solvent, as greater the dipole moment of itself is. From such a view-point, studies were also carried out by Tamamushi,[5] and Sata.[4] However, the general relation has not yet been found.

In the case of the adsorption from the solution, the phenomena depend on the combination of the solute, the solvent and the adsorbent, and the electrical natures are also affected by their combinations. So things are complex and the definite results has not been found, notwithstanding, there are many qualitative relations between the adsorption and the dielectric natures. The present author thinks that to use charcoal as the adsorbent for the sake of convenience of the experimental technique is one of the reasons for such confusions. For charcoal is a typical

(1) Debye, *Physica*, 1 (1921), 362; Lorenz and Lande, *Z. anorg. Chem.*, **125** (1922), 47; E. Hückel, "Adsorption und Kapillarkondensation," 1928, Leipzig, p. 83.
(2) Nekrassow, *Z. physik. Chem.*, **136** (1930), 18.
(3) Heymann and Boye, *Z. physik. Chem.*, A **150** (1930), 219.
(4) N. Sata, *Kolloid-Z.*, **49** (1929), 275; *J. Chem. Soc. Japan*, **53** (1932), 617.
(5) B. Tamamushi, this Bulletin, **6** (1931), 74.

non-polar substance. Considering the electrical field of the interface, more general substance must be used as the adsorbent. The famous Traube's rule, i.e. fatty acid which has longer chain will be adsorbed more from the aqueous solution by charcoal than the one which has shorter chain is reversed[6] when silica gel (polar) is used as the adsorbent and toluene (non-polar), as the solvent. Freundlich and Heller[7] have shown that trans-azobenzene is adsorbed more by charcoal from the solution in methyl alcohol than cis-azobenzene, while, cis-form is adsorbed more than trans-form by aluminium oxide from the solution in petroleum ether. It is recognised, in general, that the non-polar adsorbent, such as charcoal, adsorbs well from the polar solvent, while the polar (or hetero-polar) adsorbent adsorbs well from the non-polar solvent, and such cases are called the "polar and non-polar adsorption."

To investigate the adsorption at the solid-liquid interface, and to consider the polar and non-polar adsorption also the present author has carried out some experiments on the behaviours of the molecules at the interface between glass (hetero-polar) and benzene or toluene (non-polar). The amount adsorbed by glass, though made into the fine powder, is so small that the method of the measurement must be specially devised. For such a purpose, the float method and the surface balance analysis were applied. In the preceding paper, the behaviours of fatty acids were reported (Part I),[8] and it was also reported that the adsorption layer is one molecular in thickness in the case of palmitic acid and benzoic acid (Part II).[9]

Adsorption of Some Benzene-derivatives by the Glass Powder. Some of benzene-derivatives have large dipole moments and it is anticipated, from the electrostatic theory, that they would be readily adsorbed at the glass-benzene interface. Nevertheless, among benzoic acid, nitrobenzene, aniline and chlorobenzene which were studied by the present author, benzoic acid alone was adsorbed by the glass-benzene interface, and the other compounds were not adsorbed, or the amount adsorbed might be too small to be measured by the present method. Results are shown in Table 1 and Fig. 1.

The adsorbent was the same glass powder ("crushed" glass powder) as reported in the preceding paper (Part I), also the experimental conditions were the same. To determine the amount of the adsorption, the float method was applied. By this method, the difference of the concentration of the solution, before and after the adsorbing procedure, is determined from the change of the density, which is measured by a float. In Table 1, the notation of "Reading of Beckmann" means the arbitrary reading of the scales of a Beckmann thermometer, that indicate the temperature at which the density of the solution is identical with that of the float. The identity of this values before and after the adsorbing procedure shows that no measurable adsorption has taken place. In the case of aniline and chlorobenzene, things were just like as the case of nitro-

(6) Holmes and McKelvey, *J. Phys. Chem.*, **32** (1928), 1522.
(7) Freundlich and Heller, *J. Am. Chem. Soc.*, **61** (1939), 2228.
(8) H. Akamatu, this Bulletin, **17** (1942), 141.
(9) H. Akamatu, this Bulletin, **17** (1942), 161.

Table 1. Adsorption of Benzene-derivatives by the "Crushed" Glass Powder.

Volume of Solution (c.c.)	Weight of Adsorbent (g.)	Initial Concentration (mol/l.)	Initial Concentration Reading of Beckmann	Final Concentration (mol/l.)	Final Concentration Reading of Beckmann	Amount adsorbed by 1 g. of Adsorbent (mol)
		Benzoic acid / Benzene				
10	4.958	0.92×10^{-2}	3.200	0.28×10^{-2}	3.107	1.3×10^{-5}
10	5.003	1.84×10^{-2}	3.465	1.13×10^{-2}	3.259	1.4×10^{-5}
10	4.936	3.67×10^{-2}	4.000	2.99×10^{-2}	3.791	1.4×10^{-5}
10	4.759	7.35×10^{-2}	5.054	6.65×10^{-2}	4.854	1.5×10^{-5}
		Nitrobenzene / Benzene				
10	4.812	1.27×10^{-2}	0.933	1.28×10^{-2}	0.934	0
10	4.407	2.55×10^{-2}	1.282	2.52×10^{-2}	1.278	0
10	5.258	5.10×10^{-2}	1.978	5.11×10^{-2}	1.981	0
10	4.616	10.20×10^{-2}	3.375	10.23×10^{-2}	3.380	0

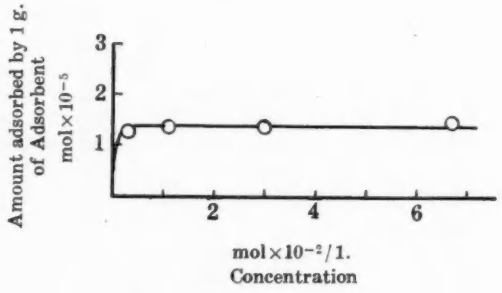


Fig. 1. Adsorption of Benzoic acid.

benzene, where the concentration of the solution which has been studied was in the region of 0.145 mol/l. and 0.089 mol/l. respectively for aniline and chlorobenzene.

Essentially, this method is not so acute when the difference of densities of the solute and the solvent is not large. However, when the densities of the compounds are much larger than benzene (solvent), it is expected that the change of the concentration would be observed acutely by measuring the density. Considering the result of the preceding paper (Part II), and the curve of Fig. 1, it is plausible to consider that the adsorption layer of benzoic acid is monomolecular in thickness. By this method, we can investigate the adsorption even when the adsorption layer is less than the monomolecular one. To make sure the above results, the adsorption measurement was carried out using the "spherical" glass powder[9] of which specific surface area has been known in the case of nitrobenzene. However, no measurable adsorption also could be found.

It seems plausible to the present author to consider that nitrobenzene, aniline and chlorobenzene are not adsorbed at the glass-benzene interface, in the region of the concentration of the solution which has been studied. This fact is also deduced by the qualitative facts which are described in the following section.

On the Lateral Movement of the Float in the Solution. By the float method of density measurement, a float which was made of a boro-silicate glass was used. It is put in the solution to be tested, and the velocity of the motion of the float up and down at a certain temperature was observed. In this experiment a peculiar behaviour of the float has attracted notice of some investigators, namely, the float moves occasionally toward the wall of the cell and attaches to it. Sometimes this may be an accident caused, for instance, by the vibration of the stirrer, or the electrical charge of the float, etc. By the present author's experiences, however, it always occurs when the liquid is non-polar one such as benzene or toluene. Robinson and Smith[11] have reported that they had been troubled by this phenomenon in the case of silicon tetrachloride. On the other hand, the float never attach to the wall in the case of benzene or toluene dissolving fatty acid, or benzoic acid, while the float attach to the wall in the case of dissolving such as nitrobenzene or chlorobenzene as well as pure benzene. To prevent this behaviour of the float, it is necessary to take care not to be clean the float or the cell too much. Usually, the float is washed with benzene freshly distilled using a Soxhlet apparatus, and the cell is washed with chromic acid mixture, then with distilled water, and dried in an electrical drying oven, at each measurement. In those cases, however, the cell must be exposed in the open air for a long time (overnight, for instance) before the use, or the washing of the float must be neglected to prevent the adhering of the float to the wall.

The cause of such peculiar behaviour of the float may be the electrical charge (by the friction, for instance), or the heterogeneous contamination at the surface of the float. During the measurement of the density by the float method, the density of the float is almost identical to that of the solution. Consequently, the float can be moved by a very small force. The nature of this force is not known yet. The float does not attach to the wall of the cell when there exists any adsorption layer at the surface of the float or the wall,—it may be solvation, the contamination or the adsorption of a certain substance from the solution. The fact that the occurrence of this peculiar behaviour of the float in benzene solution dissolving nitrobenzene or chlorobenzene, corresponds to the non-adsorption of these compounds by the glass surface.

Adsorption of Alcohols and Esters. Alcohols are also adsorbed by glass from benzene solution. The results shown in Table 2 and Fig. 2 are also obtained by the float method.

Methyl alcohol and ethyl alcohol were much adsorbed, as the concentration of the solution was increased. The behaviours of alcohols seem to be alike to the fatty acids. In the case of fatty acids, however, the adsorption takes place still in the region of the low concentration of the solution, on the other hand, in the case of alcohols, no considerable adsorp-

(10) Robinson and Smith, *J. Chem. Soc.*, **1926**, 2162.

Table 2. Adsorption of Alcohols and Esters by the "Crushed" Glass Powder.

Volume of Solution (c.c.)	Weight of Adsorbent (g.)	Initial Concentration (g./100 c.c.)	Final Concentration (g./100 c.c.)	Final Concentration (mol/l.)	Amount adsorbed by 1 g. of Adsorbent (mol)
Methyl alcohol / Benzene					
10	5.557	0.1065	0.0998	0.031	0.4×10^{-5}
10	5.615	0.213	0.190	0.059	1.3×10^{-5}
10	4.960	0.426	0.400	0.125	1.6×10^{-5}
10	5.222	0.852	0.808	0.252	2.6×10^{-5}
10	5.950	1.704	1.635	0.510	3.6×10^{-5}
Ethyl alcohol / Benzene					
10	5.657	0.0912	0.0875	0.019	0
10	5.137	0.1823	0.170	0.037	0.5×10^{-5}
10	5.607	0.3645	0.3175	0.069	1.8×10^{-5}
10	5.240	0.729	0.646	0.140	3.4×10^{-5}
10	5.103	1.458	1.365	0.296	4.0×10^{-5}
Propyl alcohol / Benzene					
10	4.811	0.266	0.265	0.044	0
10	4.693	0.532	0.530	0.088	0
10	5.307	0.761	0.752	0.109	0.3×10^{-5}
10	4.767	1.064	1.038	0.173	0.9×10^{-5}
10	5.186	1.308	1.287	0.214	0.7×10^{-5}
10	4.572	1.522	1.505	0.251	0.6×10^{-5}
10	5.080	2.128	2.125	0.354	0
Tetradecyl alcohol / Benzene					
10	5.768	0.526	0.526	0.025	0
10	5.903	1.052	1.052	0.049	0
10	5.218	2.104	2.017	0.094	0.8×10^{-5}
Butyl acetate / Toluene					
10	4.356	0.138	0.113	0.010	0.5×10^{-5}
10	4.333	0.275	0.240	0.021	0.7×10^{-5}
10	5.267	0.551	0.517	0.045	0.5×10^{-5}
10	4.942	1.101	1.080	0.093	0.4×10^{-5}
10	4.299	2.202	2.20	0.189	0
Tripalmitine / Toluene					
10	7.158	0.461	0.461	0.006	0
10	5.995	0.923	0.923	0.012	0
10	6.489	1.845	1.845	0.023	0

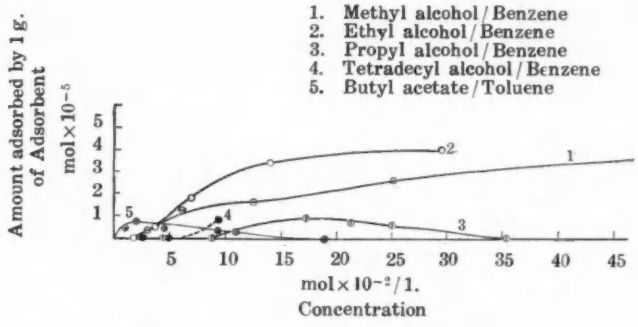

1. Methyl alcohol / Benzene
2. Ethyl alcohol / Benzene
3. Propyl alcohol / Benzene
4. Tetradecyl alcohol / Benzene
5. Butyl acetate / Toluene
Amount adsorbed by 1 g. of Adsorbent
mol × 10⁻⁵
mol × 10⁻² / 1.
Concentration

Fig. 2. Adsorption of Alcohols and Butyl acetate.

tion takes place until the concentration of the solution increases beyond a certain range. This is a remarkable fact that the range of the concentration of the solution, at which any considerable adsorption be observed, is narrow in the case of propyl alcohol, and it seems that some negative adsorption takes place at the higher concentration. For tetradecyl alcohol, this range of the concentration is also limited, because it has the limited solubility.

For butyl acetate and tripalmitine, the amount adsorbed were small. Especially, in the case of tripalmitine, the change of the concentration of the solution was not observed before and after the adsorbing procedure. However, there are many qualitative evidences to consider that tripalmitine is adsorbed. The density difference of tripalmitine and toluene is rather small, and moreover, the size of the molecule of tripalmitine is large, so the numbers of molecule necessary to cover the surface of the adsorbent will be small, and the amount of the adsorption may not be observed by this method. The surface balance analysis was used instead of the float method, since tripalmitine makes a good monomolecular film on the surface of water. Moreover, the "spherical" glass powder of which specific surface area has been known, was used as the adsorbent. The results are shown in Table 3.

Table 3.

Adsorbent: "Spherical" glass powder No. 2. (of which specific surface area is 1810 cm^2.)
Solution: Tripalmitine / Benzene.

Volume of Solution (c.c.)	Weight of Adsorbent (g.)	Initial concn. (mol/l.)	Final concn. (mol/l.)	Amount adsorbed by 1 g. Adsorbent (mol)	*Area occupied by one molecule.
5	5.328	0.44×10^{-3}	0.40×10^{-3}	0.4×10^{-7}	747 sq. Å
5	5.229	0.88×10^{-3}	0.80×10^{-3}	0.8×10^{-7}	353 "
5	4.709	1.77×10^{-3}	1.51×10^{-3}	2.8×10^{-7}	108 "

* In the tightly packed monomolecular film on the surface of water, the smallest area which one molecule of tripalmitine occupies, is about 66 sq. Å.

From this result, it seems that tripalmitine is hardly adsorbed in the region of the low concentration of the solution. But at the higher concentration of the solution, the adsorption layer approaches to the monomolecular one.

On the Surface of the Glass Powder. As reported in the preceding paper, the amount of benzoic acid adsorbed by 1 g. of the "spherical" glass powder, of which specific surface area is 4700 cm.,^{2} is determined to be about 3×10^{-6} mol. By the "crushed" glass powder, as reported in the present paper, this amount is about 1.4×10^{-5} mol. The shape of the particles of this powder are broken and irregular, and the surface area cannot be known. The particle size of this powder was estimated roughly by measuring the sedimentation velocity. As the result, it was found that the radius of the particles are distributed in the range of 3.5–7.5 micron, if the shape of the particle is assumed to be spherical. Taking the average radius to be 5.5 micron, the specific surface area is roughly assumed to be about 2180 cm.^{2} It must be deduced, from the results, that the "crushed" glass powder adsorbs benzoic acid ten times as much as the "spherical" glass powder, with the same surface area. The surface of the "spherical" glass powder went once melted through the melting process, in the course of its preparation, while the surface of the "crushed" glass powder, was left as they have been made by the crushing. The surface area of the "crushed" powder was estimated to be 2180 cm.,^{2} which was calculated under the assumption that the shape of the particle is spherical. The true surface area must be, of course, larger than this value owing to the irregularity or the brokenness. The estimation of the area, considering the geometrical shape of the particles, however, may not be larger than three or four times of the value estimated from the assumption that the shape of particles is spherical. Consequently, the two or three times out of the ten times larger adsorbability by the "crushed" powder, might be caused by the great adsorbability at the edges or the points, or otherwise, the existence of crevices and wrinkles has to be assumed. In the case of the adsorption of palmitic acid by the "crushed" powder and by the "spherical" powder, things are also alike to the case of the adsorption of benzoic acid.

It can be supposed, frequently, that the chemical as well as physical natures of the surface of glass might be varied by their treatment, for instance, natural or not (polished or melted). Nevertheless, the experimental informations are scarecely known. The adsorbability by the glass surface reported in the present paper is an example of such cases.

Note on the Results. Results investigated show that carboxylic acids are always and readily adsorbed at the glass-benzene interface, even in the low concentration of the solution. Alcohols are also adsorbed, but they are not so easily adsorbed like carboxylic acid, and the adsorption does not take place until the concentration of the solution increases beyond a certain range. Nitrobenzene, aniline and chlorobenzene are not adsorbed at the glass-benzene interface when the concentration of the solution is as large as about 0.1 mol/l. If the adsorption takes place as the result of the orientation of the adsorbate molecules at the interface, caused by the tendency of the molecules intending to moderate the potential gap, nitrobenzene, aniline and chlorobenzene will be the most adsorbable com-

pounds, since they have large dipole moments[11] or the molecular polarisations.

Considering that alcohols and esters are also adsorbed, it cannot be assumed simply that, the adsorption by glass is a kind of the chemical reaction between the acid and the base in the usual sense. It seems a certain radical of a molecule, rather than the dipole moment as a whole, that associates with the adsorption. If the molecule be adsorbed by being approached closely to the atoms or molecules of the adsorbent, the cause of the attraction will not be the moment as a whole, but the local polarity in the molecule. Then, ultimately, the force of the adsorption is not far from the valency force. Among the forces which can be considered, the attraction[12] caused by the hydrogene bridge between oxygen of glass and −OH radical, for instance, is also possible, but it is not beyond a speculation at present.

It must be noticed that, the substances which can be adsorbed by glass are rather limited and the amount of the adsorption is relatively small, while various substances are adsorbed in much quantity by charcoal, silica gel or alumina gel. It is probable that the mechanism of the adsorption is quite different for the case of the porous substance and the substance of compact surface, and it will not be caused simply by the surface area being large or small.

In conclusion the author wishes to express his hearty thanks to Prof. Jitsusaburo Sameshima for his kind guidance and encouragement. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Department of Education, to which the author's thanks are due.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

CORRECTIONS

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Page			
144	The last line of Table 1.	for	"Stearic acid/Toluene"
		read	"Oleic acid/Toluene"
145	Fig. 2.	for	"–5"
		read	"–6"

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(11) The dipole moments of benzene derivatives are as follows:—benzoic acid, 1.0; nitrobenzene, 3.90; aniline, 1.52; chlorobenzene, 1.52 ($\times 10^{-18}$ e.s.u.) (from the appendix of *Trans. Faraday Soc.*, **30** (1934)).

(12) The application of the hydrogene-bridge theory to the sorption by silica gel, was done recently by Elder and Springer. (*J. Phys. Chem.*, **44** (1940), 943.)